LEVEL Ⅱ (12)

AFGL-TR-80-0270

AD A096703

POSITIVE ION PHOTODISSOCIATION

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8 September, 1980

Final Report
Covering the period May 1, 1977 to July 31, 1980

Approved for public release; distribution unlimited

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER AFGL-TR-80-0270	2. GOVT ACCESSION NO. AD-AC96703	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) POSITIVE ION PHOTODISSOCIATION		5. TYPE OF REPORT & PERIOD COVERED Final Report. 1 May 1977 — 31 July 1980
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Robert C. Dunbar		8. CONTRACT OR GRANT NUMBER(s) F19628-77-C-0157
9. PERFORMING ORGANIZATION NAME AND ADDRESS Case Western Reserve University Cleveland Ohio 44106		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 61102F 2303G1AB
11. CONTROLLING OFFICE NAME AND ADDRESS Air Force Geophysics Laboratory Hanscom AFB, Massachusetts 01731 Monitor/John Paulson/LKD		12. REPORT DATE 8 September 1980
		13. NUMBER OF PAGES 75
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Positive ion
Photodissociation
Ion cyclotron resonance
Photodissociation spectroscopy

Fluorescence
Multiphoton dissociation

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)
Photodissociation of a variety of hydrocarbon ions and other ions of atmospheric interest was examined, both to obtain optical-spectroscopic, and also structural information. Techniques for obtaining time- and wavelength-resolved fluorescence information about ions were applied to several species. Multiphoton photodissociation of polyatomic ions with visible and infrared CW lasers was investigated.

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INTRODUCTION

   The ongoing research program in our laboratories is concerned with
developing techniques for studying ion photodissociation, and for build-
ing an understanding of the spectroscopy, dissociation chemistry, and
photochemical behavior of various classes of gas-phase ions. We have
continued with this program under AFGL support, while devoting increas-
ing attention to both technical developments and specific chemical studies
of particular relevance to ions of known or potential atmospheric import-
ance. Much of the research carried out under this contract has already
been described in the open literature, and in such cases a summary in
this Report will serve to direct the interested reader to the fuller
literature description.

I. PHOTODISSOCIATION SPECTRA OF IONS OF ATMOSPHERIC INTEREST

Ions for which successful photodissociation study has been carried out include CS_2^+, OCS^+ and SO_2^+.

Results for CS_2^+ and OCS^+ are described in publication #11. The photodissociation spectrum of OCS^+ was obtained from 370-240 nm, showing peaks at 310 nm and $\lesssim$240 nm. The peak at 310 nm is confidently assigned as the $\tilde{A}\ ^2\Pi$ ion excited state, and lies in a region which would be convenient for high resolution doubled-dye-laser investigation. The peak below 240 nm, with relatively large cross section $>5 \times 10^{-18}\ cm^2$, is not yet assigned with certainty. The initial photodissociation product was S^+, which was rapidly converted to S_2^+ by ion-molecule reaction with parent neutral.

A spectrum was obtained for photodissociation of CS_2^+ in the vicinity of 230-250 nm. The largest photodissociation cross section measured was at 230 nm, with a value of $4 \times 10^{-19}\ cm^2$. The assignment of this transition is in some doubt.

The photodissociation spectrum of SO_2^+ has not yet been published in the open literature, and is shown in Table I. It shows moderate photodissociation ($\sim 2 \times 10^{-18}\ cm^2$) near 240 nm, and also has a weak shoulder near 300 nm ($\sim 5 \times 10^{-19}\ cm^2$). If the electronic states of this ion are taken to be similar to those in CO_2^+, these two peaks might be tentatively assigned, respectively, to states $^2\Sigma_u^+$ and $^2\Pi_u^+$, but this spectrum has yet to be carefully analyzed. Again, the peak in the 300 nm region may be a candidate for tunable-laser study at higher resolution.

TABLE I

SO_2^+ Photodissociation Spectrum

pressure = 3.0×10^{-8} torr

electron energy = 11.5 ev

| $\sigma(\lambda) \times 10^{-18} \, cm^2$	λ (nm)
0.39	320
0.58	310
0.58	300
0.50	290
0.54	280
0.72	270
0.94	260
1.2	250
1.1	240
2.0	230

II. MECHANISMS OF MULTIPHOTON ION DISSOCIATION

A careful study was made (Publication #1) of the mechanism and kin-
etics of bromobenzene ion two-photon photodissociation, Eq. (1), and
quantitative agreement was found with the Freiser-Beauchamp[1] sequential
mechanism of Eq. (1),

$$C_6H_5Br^+ \xrightarrow{h\nu} C_6H_5Br^{+*} \xrightarrow{h\nu} C_6H_5^+ + Br \qquad (1)$$

$$\underset{M}{\overbrace{\qquad\qquad}}$$
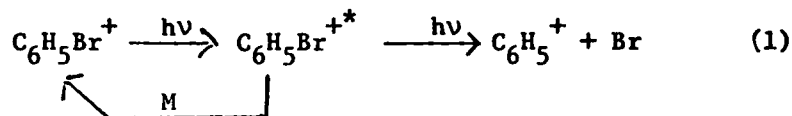
where the species $C_6H_5Br^{+*}$ represents a vibrationally excited ion resulting
from rapid internal conversion of the initial electronically excited ion
resulting from photon absorption; and M represents a neutral molecule
which can collisionally relax this intermediate species. (Recently it has
become clear that infrared radiation relaxation can also be significant.)
The sequential mechanism is of particular interest for photodissociation
processes in environments of modest light flux, such as the solar-irradi-
ated atmosphere, since it offers a mechanism for dissociating ions or
molecules of high stability by multiple absorption of photons, without
the necessity of extremely intense fluxes required by simultaneous multi-
photon processes. However, the sequential mechanism requires many internal
degrees of freedom for energy storage, and is thus probably relevant only
to polyatomic molecules.

Reported in publication #13 is a study of photodissociation of naphtha-
lene ion

$$C_{10}H_8^+ \xrightarrow{h\nu} C_8H_6^+ + C_2H_2. \qquad (2)$$
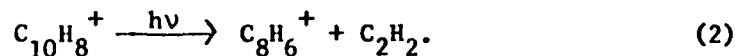
This process is a sequential two-photon process in the UV, showing the

normal I^2 light intensity dependence. However, near 600 nm the process is a <u>four</u>-photon dissociation, and thus forms a valuable link between the two-photon processes which have been studied in some detail, and the many-photon infrared photodissociation processes now being widely investigated. It had been expected that this four-photon dissociation would show an I^4 intensity dependence and a strong pressure dependence, but in fact the intensity dependence varies from $I^{1.5}$ to $I^{2.5}$ at laser powers available to us. Careful working out of the mechanism, and extensive computer simulations, have shown that these are indeed expected results, and that weak intensity dependences are to be expected in many sequential multiphoton processes. A further interesting conclusion arises from the observation that the multiphoton photodissociation rate in naphthalene ion shows only a very slight pressure dependence, and we have interpreted this as indicating that infared radiative cooling of photoexcited ions is an important relaxation mechanism, competitive with or faster than collisional relaxation.

A major study of the photodissociation behavior of halogen-substituted benzene ions was reported in Publication #14. Of particular interest was the two-photon photodissociation behavior observed not only in bromobenzene ion, which was previously known, but also in chlorobenzene and iodobenzene ion. For the latter ion, the two-photon process was rapid enough to permit use of the arc-lamp source: this is the first non-laser two-photon ion dissociation experiment we know of. Photodissociation spectra were obtained for all from halobenzene radical ions, and a seemingly satisfactory interpretation was developed in molecular orbital terms.

Repeated efforts to observe two-photon dissociation of CS_2^+ via a sequential, double $\tilde{X} \rightarrow \tilde{A}$ excitation near 500 nm have not yielded observable dissociation. It seems likely that the quantum yield for $\tilde{A}$ state fluorescence is near unity so that too little internal conversion occurs for a

sequential two-photon process.

In an important new development in multiphoton ion photochemistry, we have observed the photodissociation of the iodobenzene cation ϕI^+ by a combination of visible and infrared radiation, in a process which involves both IR and visible photons (Publication #22). This is analogous to the recent observations of Beauchamp's group of sequential multiphoton infrared dissociation of a number of ions by modest-power CW infrared radiation, but the more complex process we have observed, involving visible radiation as well as IR radiation, gives more powerful insights into the intramolecular and intermolecular energy flows in the ions under irradiation. Under infrared irradiation alone, ϕI^+ gives no dissociation – we believe this reflects the high dissociation threshold (3eV) which is difficult to reach by sequential multiphoton IR pumping. Under visible radiation alone, ϕI^+ dissociates by the well-known Freiser-Beauchamp two-photon mechanism, in which the intermediate

$$\phi I^+ \xrightarrow{h\nu} \phi I^{+*} \xrightarrow{h\nu} \phi^+ + I \qquad (3)$$
$$\overset{\curvearrowleft}{\underset{M}{\rule{2cm}{0pt}}}\rfloor$$
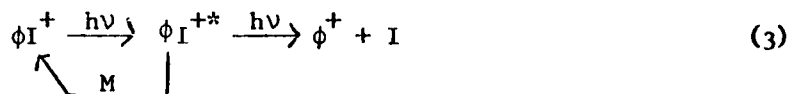
ϕI^{+*} species is a vibrationally excited ion which can be relaxed by collision with neutrals M. Infrared radiation in addition to visible radiation greatly enhances the rate of dissociation. Evidently the infrared radiation provides an efficient method of populating the ϕI^{+*} state, giving the two-laser process

$$\phi I^+ \to \xrightarrow{IR} \to \phi I^{+*} \xrightarrow{h\nu} \phi^+ + I \qquad (4)$$
$$\overset{\curvearrowleft}{\underset{M}{\rule{2cm}{0pt}}}\diagup$$
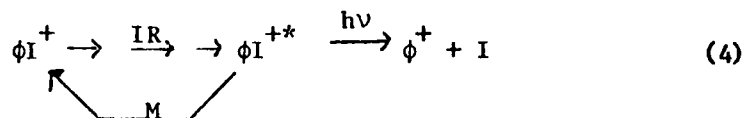
Extensive computer modelling has given quantitative support to this mechanism, and gives quantitative values (or ranges of values) for the various

optical excitation and collisional relaxation cross sections.

Using the fast ion beam spectrometer at Stanford Research Institute in collaboration with M.J. Coggiola, P.C. Cosby, J.T. Moseley and J.R. Peterson, the Principal Investigator participated in a series of experiments on the infrared-laser photodissociation of several ionic species, including CF_3I^+, $C_2F_5I^+$, $C_3F_5I^+$, and $C_6F_6^+$. Dissociation was observed when the fast ion beam interacted with light from a single-mode, line-tunable CW CO_2 laser. Preliminary analysis[2] indicates that the observed process was absorption of a single IR photon by ions emerging from the ion source with nearly enough internal energy to bring about dissociation. The cross sections show large wavelength variations, interpreted as reflecting the IR absorption spectrum of the ion. Data were also obtained on the dissociation rate and kinetic energy release, and analysis of the photodissociation process in terms of an RRKM statistical model seems to be compatible with the data for the larger ions but not for CF_3I^+. These results are particularly interesting in relation to understanding infrared multiphoton processes, since the events occurring in these fast-beam dissociations can be regarded as equivalent to absorption of the last photon in a multiphoton dissociation, followed by fragmentation. It is therefore significant to find the strong wavelength dependences observed which indicate that the IR absorption properties of the highly excited ions are not greatly different from those of ground-state ions.

III. VIBRATIONAL ENERGY TRANSFER IN ION-MOLECULE COLLISIONS

The sequential two-photon photodissociation process offers a unique opportunity for measuring the rate of vibrational energy transfer from vibrationally excited ions of well characterized internal energy. In the study reported in publication #10, the ion chosen for study was bromobenzene, which undergoes the sequential two-photon dissociation process described in Eq. (1) above. The species $C_6H_5Br^{+*}$ is now generally accepted to be a vibrationally excited ion which can store the energy ($\sim$2.5 eV) of the first photon in vibrational degrees of freedom for as long as a second, awaiting arrival of the second photon. During this period of energy storage, the $C_6H_5Br^{+*}$ can be quenched by collision with neutral molecule M. The kinetics of (1) have been worked out, so that it was possible simply by varying the nature of M to compare the collisional quenching efficiencies of various neutral molecules. Furthermore, since the collision rate for orbiting collisions is known, it is easy to calculate the number of collisions with a particular M required to quench the $C_6H_5Br^{+*}$ to an energy below the photodissociation threshold. Quenching rates and quenching collision numbers for various M species are as shown in Table II.

It is most noteworthy that the quenching efficiencies are low (with the exception of bromobenzene as collision partner, for which the resonant charge transfer

$$C_6H_5Br^{+*} + C_6H_5Br \rightarrow C_6H_5Br^* + C_6H_5Br^+ \qquad (5)$$
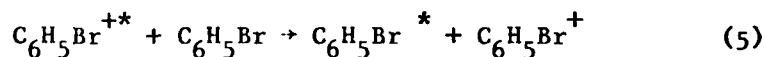
provides a highly efficient quenching mechanism). The inefficiencies of vibrational energy transfer shown by these results are surprising, although recently other data has appeared suggesting similar inefficient energy transfer for O_3^- in O_2. In spite of the intimate and strong interaction

implied by an orbiting ion-molecule collision, vibrational excitation is apparently shared to only a small extent with the neutral collision partner. Only for neutrals with many internal degrees of freedom does the quenching rate appear to become at all comparable to the collision rate.

TABLE II

Bromobenzene Ion Collisional Quenching

Neutral Molecule	Quenching Rate $(10^{-9} cc/mol.sec)$	Collision Number
CO_2	$\leq .05$	≥ 10
CH_4	$\leq .02$	≥ 50
C_3H_8	$\leq .05$	≥ 20
SF_6	.074	8
C_6H_6	.25	4
C_6D_6	.22	5
$C_6H_5NO_2$	$\leq .05$	≥ 30
C_6H_5F	.46	3
C_6H_5Br	1.5	1

IV. TRAPPED-ION PHOTOFRAGMENTATION

The photodissociation of methyl chloride ion was investigated as a favorable case for developing techniques for finding the kinetic energy and angular distribution of photodissociation products (Publication #5). The CH_3^+ product ions are formed with substantial kinetic energy at 366 nm, and with highly anisotropic angular distribution. The techniques developed for use in the trapped-ion ICR cell make use of the inherent anisotropy of the ICR ion trap: with CH_3Cl^+ ions trapped in the cell, the CH_3^+ ions produced during irradiation are detected either using the ICR detection technique to observe ions remaining in the cell, or alternatively using electrometer detection of the ions striking the cell plates. For methyl chloride ions these techniques were successful, and yielded quantitative kinetic energy and angular distribution results. The chief problems with this approach are, first, that fragement ion kinetic energies of tenths of an eV are required, and second that in the far UV production of photo-electrons becomes a serious interference. Within these limitations, ion photofragmentation studies in the ICR ion trap will be useful for investi-gating the detailed mechanism of ion fragmentation.

A photofragmentation study of COS^+ using similar techniques, descri-bed in publication #11, was made. The fragmentation to S^+ + CO proceeds with the release of .55 eV of kinetic energy. There is little, if any, angular anisotropy, which suggests that dissociation is slow compared with ion rotation.

The parent ions of butyrophenone (publication #8) and t-butylbenzene (publication #19) were studied to determine the initial photoproducts and to elucidate the subsequent ion-molecule photochemistry. These ions were of particular interest because in each case there was reason to suspect that

only a single photoproduct was formed (the most energetically favored pro-
duct in both cases) at all wavelengths examined. These studies gave us a
clear demonstration that the steady-state ICR photodissociation methods
used in prior work on these systems are unreliable in investigating complex
ion photochemistry. The substantial effort we have put in to convert our
instrument to pulsed ICR photodissociation methods was shown to be amply
justified by the excellent results we obtained in these studies.

V. PHOTODISSOCIATION SPECTROSCOPY: CONVENTIONAL AND LASER SOURCES

The spectroscopy of radical ions of substituted benzenes has received substantial attention. Spectra were reported (Publications #2 and #3) of the entire series of methylbenzene ions, with attention to determining the small substituent perturbations of the positions and intensities of the $\pi-\pi$ transition near 400 nm and the $\pi-\pi^*$ transition near 270 nm. First-order perturbation theory was found to account well for the $\pi-\pi$ substituent effects, but within a perturbation-theory framework the $\pi-\pi^*$ band showed more complex substituent shifts. Spectra were also reported for several monoalkyl benzene ions, where it was suggested that a new side-chain-to-ring charge-transfer transition becomes important in the visible for larger alkyl groups (Publication #15). A study of the spectroscopy of halogen-substituted benzenes, using one- and two-photon photodissociation techniques, was reported (Publication #14). The lone-pair orbitals of all the halogens except fluorine play a prominent spectroscopic role, with the visible-region spectroscopy being quite different from that of benzene ions with weakly-interacting substituents. By contrast, adding a methyl group to a halogen-substituted benzene ion gives no significant change in the spectrum. In Publication #6, spectra of several styrene ion derivatives were reported. The spectroscopy of these ions seems well accounted for by a picture involving strong interaction between the ring and the ethylene side chain.

Spectra of alkane and cycloalkane ions from C_5 to C_{10} show strong photodissociation in the visible region (Publication #16), attributed to the overlapping of numerous electron-promotion transitions carrying electrons from the dense set of high-lying occupied C_{2p} orbitals into the half-filled highest orbital. MINDO/3 molecular orbital calculations were

quite successful in accounting for the overall features of the spectra, and for the differences between photodissociation and photoelectron spectroscopic envelopes observed for the C_{2p} band. The strongly colored nature of the alkane radical ions is one of the most striking illustrations of the difference between the spectroscopy of neutral molecules and their parent radical cations.

The spectrum of 1,3,5-hexatriene ion was reported in Publication #4 both at low resolution across the visible/UV, and also at higher resolution in the visible, where there is well resolved vibrational structure. Identical spectra were obtained for cis and trans precursor neutrals, in interesting contrast to the observation of distinct cis and trans spectra in emission. The photodissociation spectrum appears to be that of the cis isomer, and a rearrangement of trans to cis seems a possible explanation of these observations. Allan, Dannacher and Maier[3] have argued that the dissociation of $\tilde{A}$ state cis isomer proceeds by a cyclization which is not accessible to the trans isomer; thus photoexcited trans isomers might rearrange to cis, but would not dissociate, and no photodissociation features corresponding to the trans emission would be seen.

A series of photodissociation spectra of protonated α,β-unsaturated ketone ions has been completed. The spectra are closely similar in shape to the neutral molecules, but with a constant wavelength shift, a result which is very interesting in terms of understanding substituent effects on energy levels of this ionic chromophore. This study, publication #23, is reproduced as Appendix A.

VI. ION STRUCTURES AND REARRANGEMENTS

A study of isomeric $C_3H_5Cl^+$ ions by tuned-laser photodissociation spectroscopy was reported in publication #7 which has far-reaching implications for the study of ion structures and ion-molecule reactions by photodissociation techniques. Four isomers of $C_3H_5Cl^+$ were unambiguously distinguished by their resolved vibrational structure. Using their characteristic high-resolution photodissociation spectra, it was then possible to determine the product-ion structures for the ion-molecule reaction

$$C_3H_7Cl + C_3H_6^+ \longrightarrow C_3H_5Cl^+ + C_3H_8 \tag{5}$$
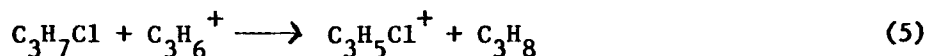
for different isomeric C_3H_7Cl precursors. This demonstrated capability for using high resolution laser photodissociation as a detailed probe of mechanisms of ion-molecule reactions is an important new research tool.

Photodissociation spectroscopy has been applied as a tool for studying structural rearrangements in a number of hydrocarbon ions. Attention has been given to rearrangements involving double-bond shifts, electrocyclizations, cis-trans isomerizations, and more drastic rearrangements in both radical ions and protonated molecules. Publication #6 describes the photodissociation chemistry of styrene ion and several of its derivatives and isomers. A number of rearrangement pathways of the ions were mapped out, and substantial additions were made to an understanding of the excited electronic states of hydrocarbon radical ions.

It is found, for instance, that the parent ions of styrene, (I), cyclooctatetraene (II) and barrelene, (III), all $C_8H_8^{+\cdot}$ isomers, do not
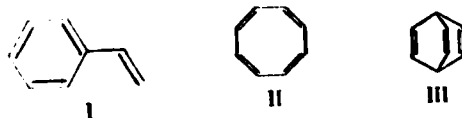
interconvert on a time scale of seconds, whereas the $C_8H_9^+$ ions obtained by protonating these same neutral molecules all rearrange to the styryl ion structure.

There has been recent attention to the question of migration of double bonds into conjugation. In several ions, for instance 3-phenylpro-pene (Publication #6) and 1,4-hexadiene,[4] the double bonds were shown by the photodissociation spectra to migrate to give exclusively ions of con-jugated structure, in these cases β-methylstyrene ion and 2,4-hexadiene ion (Publication #24). However, in several instances where the double bond would have to move by more than one position to reach conjugation, such as 1,5-hexadiene, 1,7-octadiene, and 4-phenyl-butene, the spectra showed that no rearrangement takes place. It was also found from laser photodissociation spectra that interconversion of the three cis/trans isomers of 2,4-hexadiene ions does not take place on a time scale of seconds. Publication #24 (reproduced as Appendix B below) describes the work on hexa-diene ions in detail.

The electrocyclic ring-opening-ring-closing interconversion between 1,3,5-hexatriene and 1,3-cyclohexadiene ions was investigated by photodisso-ciation spectroscopy (Publication #20), and it was found that no intercon-version takes place in seconds. It was noted that this is a case where the concerted process is forbidden by orbital symmetry conservation (and by electronic state symmetry correlation), so that the interconversion might be expected to be unfavorable. This system has also been studied in low-temperature solid matrix,[5] where the thermal rearrangement was also found not to occur. In condensed phase, it was also possible to look for the allowed photochemical interconversion of the ions, and interconversion was, in fact, observed.

VII. ION FLUORESCENCE

Work was undertaken in collaboration with Dr. David Turner in his laboratory at Oxford University on various aspects of the fluorescence of various ions following excitation by HdIα radiation. Publication 21 describes results obtained for photoionization-induced fluorescence of gas-phase CN-containing ions. This work was stimulated by observation of intense CN-radical fluorescence from acetonitrile under HeIα radiation, which was suspected to follow dissociative photoionization. However, attempted observation of the CN emission in coincidence with CH_3^+ photoproduct ions was unsuccessful, and it was concluded that in acetonitrile, and probably also in several other fluorescing nitriles, the CN emission corresponds to a non-ionizing neutral dissociation channel. However, the pentafluorocyano-benzene molecule was found to give a broad fluorescence band which is confidently assigned as molecular-ion fluorescence.

A photon-photoion coincidence experiment was undertaken, using a mono-chromator to disperse the ion fluorescence emission, with the primary purpose of measuring the fluorescence lifetimes of mass-analyzed gas-phase ions as a function of emitted photon wavelength.

Excited-state ions were produced by HeI (21.2 eV) photoionization of the neutral gas. Fluorescent emission from the ions was monitored through the monochromator ($\sim$2 nm resolution), and when a photon arrival was detected, the ion responsible was detected in delayed coincidence, with mass dis-crimination through its time of flight following photon arrival. The spread of ion arrival times for a given mass can be analyzed to yield the fluor-escence decay curve for the ion. The apparatus developed was unique in some respects, and a detailed description will appear.

the relatively poor signal/background ratio and low count rate
for the coincidence experiments precluded, for CO_2^+ in particular, the
goal of accurate fluorescence lifetime measurements at a large number of
well resolved wavelengths, and accordingly an alternative method was used
to extend and improve the data. A strong electric drift field applied to
the ions formed in the HeI beam moved the ions rapidly into a collector
electrode on a time scale comparable to the fluorescence time scale.
Fluorescence is thus in competition with ion destruction, and the extent
of fluorescence quenching as a function of electric drift field strength
can be analyzed in terms of the ion lifetime.

These ion drift measurements were not designed for reliable absolute
lifetime measurement, but for CS_2^+ in particular with its very long life-
time, this method is nevertheless of considerable value. Lifetime values
were obtained for four ions: N_2^+ at 391 nm gave a value of 46 msec, compared
with the known value[6] of 60 nsec for $\tilde{B} \, ^2\Sigma_u^+$ (v=0) $\rightarrow \tilde{X} \, ^2\Sigma_g^+$ (v=0). For
$\tilde{N}_2O^+ \, A^2\Sigma^+$ 9v=0) $\rightarrow \tilde{X}^2\Pi$ (v=0) at 357 nm, a value of 216 $\pm$ 20 nsec was measured,
and the v=0 to v=1 peaks are the same within the uncertainties, as would
be expected for transitions originating from the same upper state, and
are in agreement with the literature value[7] of around 230 nsec. The average
of all the CO_2^+ values is 113 nsec.

The lifetime of CS_2^+ is of most interest, since it is so exceptionally
long, and is poorly known. The average of all the points in Fig. 2 gives
a value of 3.5 μsec for the average $\tilde{A}$ lifetime, with an estimated uncer-
tainty of 15%. This is close to Eland et al.'s value[8] of 4 μsec, but is
more precise; it is also close to the estimate of 4 μsec which Bondybey and
Miller derive from matrix isolation results.[9]

The absolute lifetimes measured by this method seem worthy of
reasonable confidence within an uncertainty of perhaps $\pm$ 15%. This method
clearly has promise for species like CS_2^+ where the lifetime is inconven-
iently long for other gas-phase techniques.

The lifetime for CO_2^+ (A→X) emission was measured at 33 points between
350 and 420 nm, as shown in Figure 1. The emission spectrum of CO_2^+ , also
shown in the Figure, is similar to that reported by Lee and Judge,[10] and
their assignment, derived from the higher-resolution work of Wauchop and
Broida, is indicated. As is seen in the Figure, prominent peaks are seen
corresponding to sequences in two progressions, the (V',0,0) → (V'+ΔV,0,0)
progression, and the (V',0,0) → (V'+ΔV,0,2) progression. The lifetime
measurements are seen to sample points in about eight different sequences,
at a resolution good enough to provide at least partial separation of the
individual vibrational transitions within the sequences. The notable
result is that there is no significant variation in fluorescence lifetime
across this range or across the individual sequences, and the data clearly
rule out large systematic variations in lifetime as a function of V' value.
The emission lifetime therefore does not depend strongly on the vibrational
level from which the transition originates.

Figure 2 shows the fluorescence and lifetime spectra obtained for CS_2^+.
The fluorescence spectrum, apparently the first reported with HeI excitation,
is similar to that obtained and assigned by Lee and Judge[11] using 923Å ioniz-
ing excitation, although the resolution is lower. Lee and Judge give a
tentative assignment based on the progression $\tilde{A}^2\Pi_u$ (V',0,0) → $\tilde{X}^2\Pi_g$ (V'+ΔV,0,0),
each peak being spin-orbit split by approximately 8 nm. This assignment
puts the 0→0 ($\Omega = \frac{3}{2}$) transition at 488.0 nm, and the 0→0 ($\Omega = \frac{1}{2}$) transition
.. 494.0 nm.

The fluorescence lifetime spectrum of Fig. 2 shows variations greater than statistical scatter. There is a definite, statistically significant trend toward short lifetimes at the peaks in the emission spectrum near the short-wavelength end of each sequence. It appears that different vibrational levels of the $A^2\Pi_u$ level have different fluorescence lifetimes, and a consistent interpretation can be made assuming that the low v' levels of $A^2\Pi_u$ (v' 3) have lifetimes significantly shorter than the average. However, to say more than this, data of much higher wavelength resolution and statistical precision will be needed.

The present wavelength resolved lifetime measurements provide an interesting complement to photoelectron coincidence measurements such as those of Bloch and Turner.[12] In the latter experiment, the emitting ion is selected in a known V' state by coincidence with the high resolution photoelectron spectrum, and then the average liftime for fluorescence emission at all wavelengths is measured. Thus the initial state of the excited ion is known, but the observed fluorescence emission may be direct from this state, or may be complicated by cascading among the excited-state vibrational levels prior to emission. The wavelength-resolved emission lifetime measurements, on the other hand, measure the lifetime of a particular V' level, which will reflect not only the radiative lifetime of the level, but also the cascading processes which populate and deplete this level. If interconversion among different V' levels of the excited state is negligible, the two measurements should give the same results, while it interconversion is important, they will provide complementary sets of information on these processes. Unfortunately, photoelectron coincidence data on these ions at high resolution are not yet available.
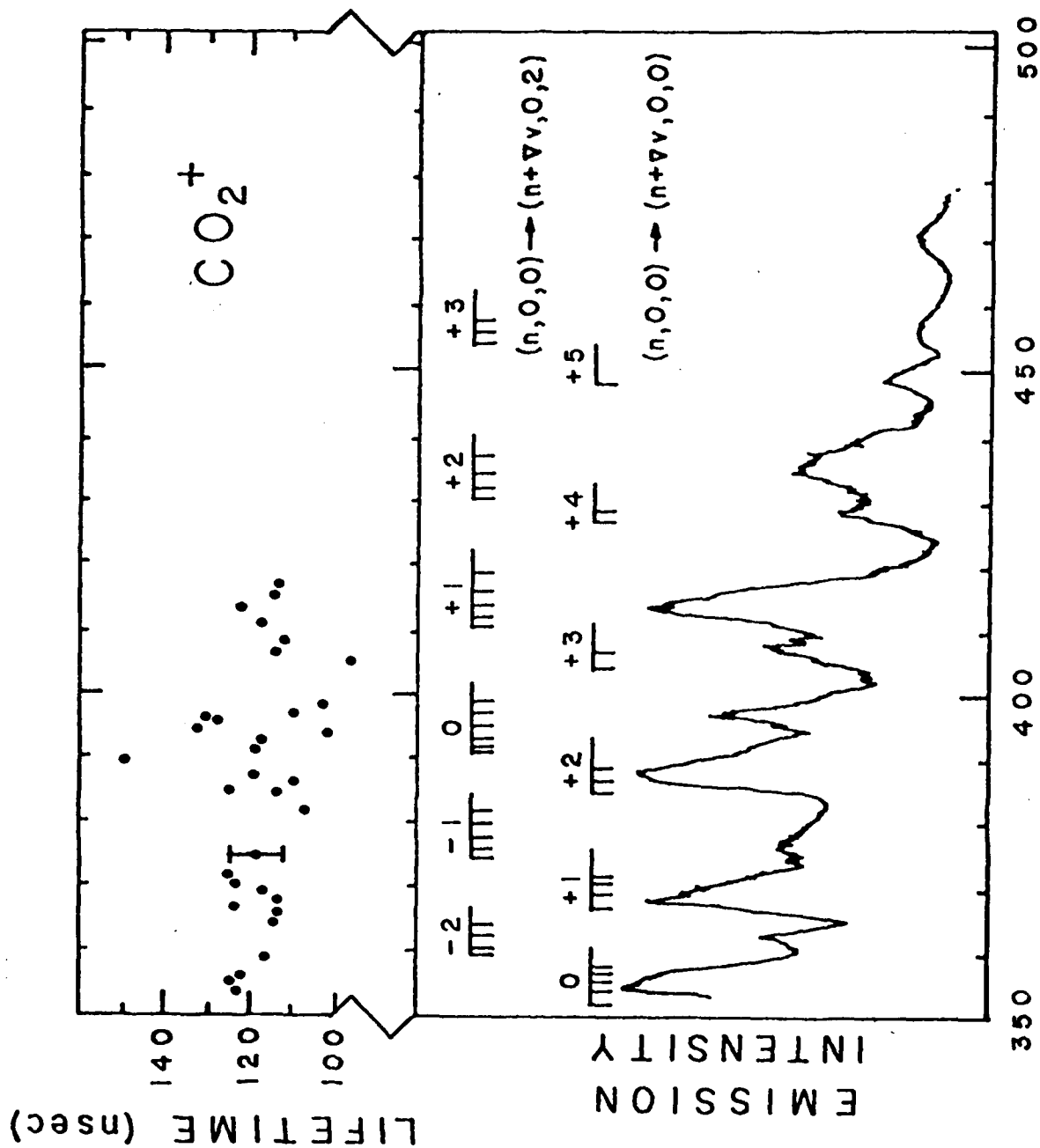
Figure 1. Emission spectrum (lower) and fluorescence lifetime spectrum (upper) of CO_2^+. Two progressions are labeled in the emission spectrum, with the small numbers above each of the sequence designations being the values of Δv.
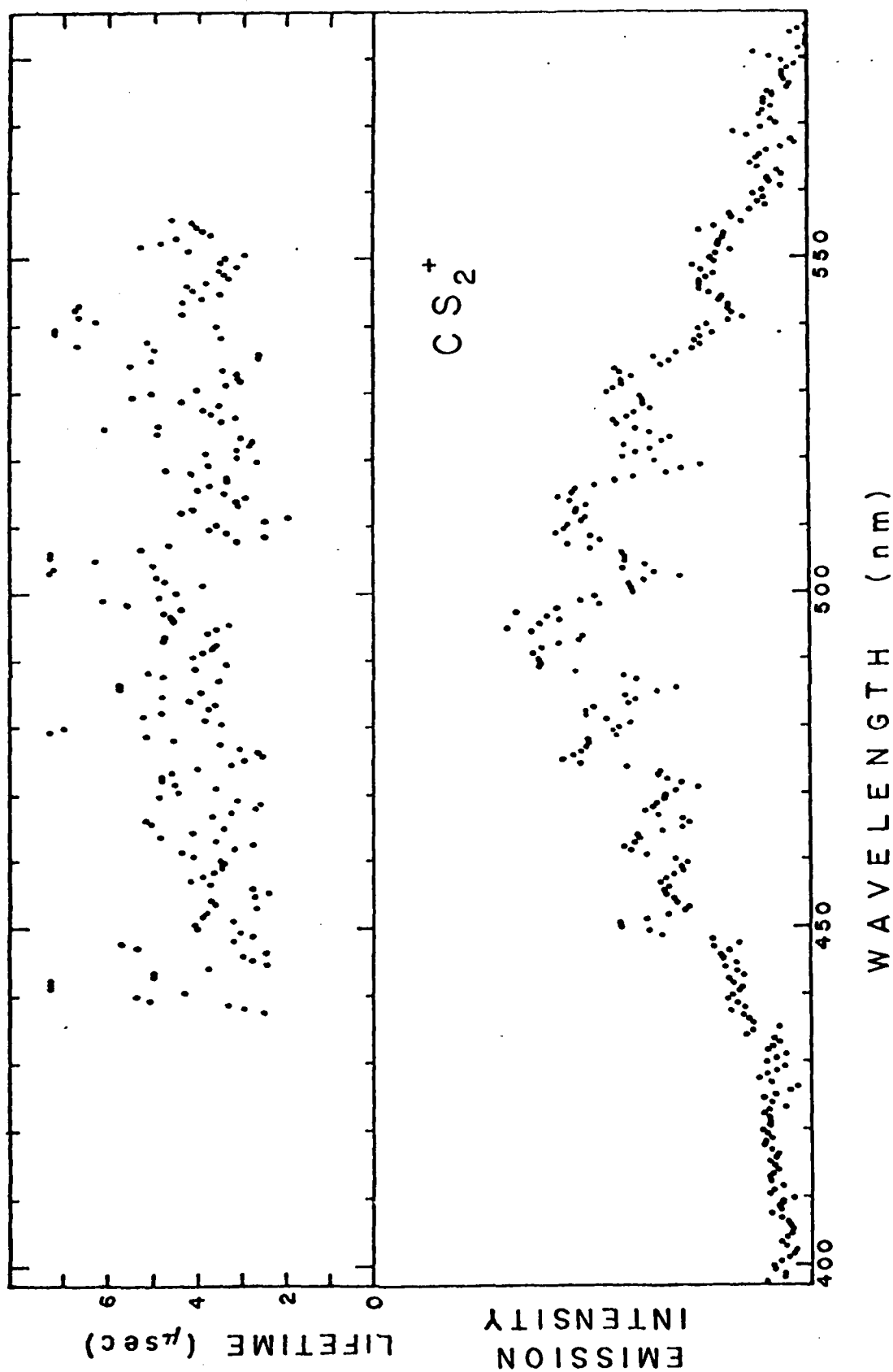
Figure 2. Emission spectrum (lower) and fluorescence lifetime spectrum (upper) for CS_2^+.

The lack of variation in lifetimes of various V' levels of the $\tilde{A}$ state of CO_2^+ may reflect either coincidental similarity in the radiative rates for these different levels, or it may reflect rapid interconversion among different V' levels so that a given ion rapidly transfers energy among its different vibrational modes. No choice can be made between these possibilities, but in the case of CS_2^+, the non-uniformity of the observed lifetimes indicates that vibrational levels of the $\tilde{A}^2\Pi_u$ state are not in rapid equilibrium with each other on a time scale of microseconds.

VIII. MISCELLANEOUS RESEARCH PUBLICATIONS

A theoretical investigation was completed on the coupling of the ion cyclotron motion with internal angular momentum of an ion moving in a magnetic field. It was concluded that shifts and splitting of the ion cyclotron resonances can occur by coupling to rotational degrees of freedom of the ion, although these effects are negligible except in the case where the cyclotron frequency matches the energy of a rotational transition. It was suggested that high resolution ion cyclotron resonance spectroscopy could exploit these phenomena to identify low-frequency rotational transition of radical ions. (Publication #9).

Several review articles concerning various aspects of the interaction of light with gas-phase ions were prepared during this period (Publications #12, 18 and 25).

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APPENDIX A

PHOTODISSOCIATION SPECTROSCOPY OF GAS-PHASE

PROTONATED ACROLEIN DERIVATIVES

by

Jeffrey P. Honovich

and

Robert C. Dunbar

Abstract

The low resolution photodissociation spectra of a series of α,β unsaturated aldehydes and ketones have been obtained using ion cyclotron resonance techniques. Comparison of these spectra with the absorption spectra of the corresponding neutrals yields the acid-base properties of the $'\pi\pi*$ excited state in terms of a change in proton affinity (ΔPA) upon excitation. The results concern the effects of methyl groups and extended conjugation on the proton affinity of the $'\pi\pi^X$ state of the parent acrolein chromophore. Some of the ions in this study are compared with solution spectra to determine the effects of solvation. The results of several theoretical calculations are examined in terms of excited state properties and compared with our ΔPA interpretations. The noted similarities and differences between ion and neutral indicate that a set of modified Woodward rules would be appropriate for this class of ions.

Introduction

Compared to the physical and chemical knowledge of neutral species, our understanding of the corresponding ions is far less complete. Advances in experiment and theory are now allowing many of the approaches worked out for characterizing neutrals to be applied to these less familiar compounds. Of particular interest to us has been the recent emergence of optical-spectroscopic means of studying gas-phase ions made possible by the technique of ion cyclotron resonance photodissociation spectroscopy (ICR-PDS). We describe here a study of a series of protonated α,β-unsaturated aldehydes and ketones by this technique where the results have connections to the well-established spectroscopy of the corresponding neutrals.

The influence of substituents on the π-π^* transitions in neutral chromophores is documented in large detail, with some of the regular and systematic effects being codified in the empirical Woodward rules.[1] As yet, no sufficiently extensive series of gas-phase ions has been examined to assess how these quantitative and qualitative regularities carry over to the ions. The protonated acrolein chromophoric group was chosen for such a study, with the hope that protonation of the oxygen would not disturb the neutral chromophore beyond recognition, so that comparison with the well understood neutrals would be possible as a reference.

Experimental Technique

Due to the difficulty in obtaining large enough concentrations of
gas phase ions for normal absorption spectroscopy, the indirect method of
photodissociation spectroscopy (PDS) was employed as the route to obtaining
spectroscopic information. As details of icr spectroscopy are given else-
where,[2] only a brief description will be presented below. The icr instrument
represents a specialized mass spectrometer which functions to generate ions,
trap them on a time scale of seconds via crossed electric and magnetic fields
and finally detect them according to their m/z ratio. During the trapping
period the ions are irradiated with wavelength-selected light. If absorption
occurs and the ion reaches either directly or indirectly a dissociative state,
the result will be a decrease in the population of the absorbing ions. By
monitoring the disappearance of a specific ion and normalizing for irradiation
time and intensity, one obtains a photodissociation cross-section (σ), which
when plotted as a function of irradiation wavelength, yields the photodisso-
ciation spectrum of the ion. Anything observed by this method represents
at most the lower limit of the absorption spectrum of the ion, since photo-
dissociation may be in competition with non-dissociative relaxation processes
such as fluorescence.

The instrumentation consisted of a Varian ICR-9 spectrometer which has
been modified for pulsed mode operation. The photon source was a 2.5 kw
Hg/Xe arc lamp and a Schoeffel monochromator. Resolution (FWHM) was of
14 nm except for compound #3 (7 nm), while in each case the region near
the peak maximum was rescanned at 7 nm resolution to assign λ_{max} more pre-
cisely. All samples were commercially available and used without further
purification. The protonated ions were generated in a low-pressure chemical

ionization fashion using water or phosphine as reagent gases. Samples were typically 1×10^{-8} torr with about ten times excess protonating agent. Trapping time for the ions was around 4 seconds. The spectra presented represent averages of several sets of data.

Results

Figures 1-7 show the photodissociation spectra obtained for the series of protonated substituted acroleins along with the UV spectra of the corresponding neutrals. The vertical scales have been arbitrarily adjusted to give the same height for both ion and neutral. Since the photodissociation spectra are taken in gas phase, it is desirable to use gas phase conditions for the neutral spectra. Due to low vapor pressure and impurities in some of the samples the gas phase bandshapes were sometimes difficult to discern, so spectra taken in cyclohexane were used, with the spectrum shifted to make λ_{max} correspond to its gas phase value, as measured in this lab. The gas phase value for 1 had to be estimated from its solution value by comparison with solvent effects on compound 2.

Included for some ions are absolute photodissociation cross sections obtained by comparison with a known standard under identical conditions. In these experiments, where protonated ions are being formed while concurrently being dissociated, the average irradiation time has been taken to be equal to half the trapping time. To correct for this the observed cross-sections were doubled to give the reported values. The results are summarized in Table I.

Discussion

From figures 1-7 it is apparent that the spectra of the protonated ions are similar to those of the neutrals but for a shift in wavelength. This behavior has been noted in other studies of protonated ions.[3] It is generally accepted that protonation occurs at the oxygen atom in both solution[4] and gas phase[5] for the simple unsaturated carbonyls. As protonation does not change the number of electrons, it may as a first approximation be considered as a perturbation of the acrolein chromophore. Therefore, the transition observed in the ion is analogous to the $\pi \to \pi^*$ excitation seen in the normal UV spectra of the neutrals. In all cases a substantial red shift occurs upon protonation.

Following the analysis of Freiser and Beauchamp[3], this shift can be related to the change in proton affinity (PA) of the base upon excitation. The scheme is illustrated below

$$B^* + H^+ \xleftarrow{\text{PA(B*)}} (BH^+)^*$$

$$\uparrow E_1 \qquad \uparrow E_2$$

$$B + H^+ \xleftarrow{\text{PA(B)}} BH^+$$
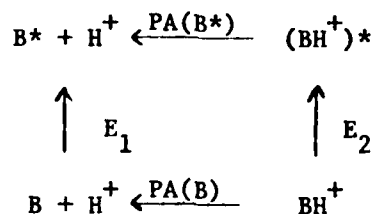
where E_1 is obtained from the UV spectrum of the neutral and E_2 from the photodissociation spectrum of the ion, with B* and (BH)* representing the π^* state of the neutral and protonated base respectively. Equating the two pathways from BH^+ to $B+H^+$ and rearranging gives

$$E_1 - E_2 = PA(B^*) - PA(B) = \Delta PA.$$

Although the absolute ground state PA's are not available, the difference in transition energies (E_1-E_2) gives the excited state proton affinity relative to that of the ground state (ΔPA).

Strictly speaking the (E_1-E_2) values should be taken from 0-0 adiabatic energies but, when both the ion and neutral have similar band shapes, it has been considered reasonable to use λ_{max} values without introducing much error.[3] Since all the compounds studied are substituted acroleins, these results survey the effects of methyl substituents and extended conjugation on the ground and excited state acid-base properties of this chromophore.

As tabulated in Table I, the ΔPA values range from 1.1 to 1.7 eV over the series. This is a basicity increase of at least 18 pKa units and suggests a large charge redistribution upon excitation. Based on the compounds and ΔPA values, the results can be divided into three groups. Compounds 1, 2 and 3 have similar values indicating that methyl substitution on the α and β positions has little effect on ΔPA. Compounds 4 and 5, in which conjugation has been extended, show somewhat larger values of ΔPA which are similar to each other. Finally compounds 6 and 7 incorporate a phenyl ring, but in doing so admit the change of alternate protonation sites, since the typical proton affinity of the substituted benzene ring is high enough to make protonation there possibly competitive with oxygen protonation. Considering the similarity of the neutral spectra of 6 and 7, one would expect similar ion spectra: the double peak in 7 may be matched with the indication of two peaks in 6, but the dissimilarity in λ_{max} values for the shorter wavelength feature is not easily accounted for. It is simply unclear which of the features in these two spectra reflect a structured optical spectrum and which may arise from contributions for ring-protonated species.

The differences noted in the ion spectra of 6 and 7 indicate that the methyl group in 7 has a more significant effect on ΔPA than methyl substitution on compounds 1, 2 and 3.
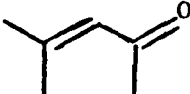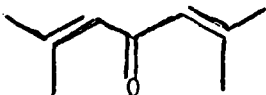
One presumption of the above excited state analysis is that protonation must not fundamentally alter the chromophore. The similarity in substituent effects and bandshapes between ions and neutrals seems to bear this out. A possible disruptive effect on the electronic nature of the chromophore would be protonation to form a hydroxy-allyl system illustrated by structures b and c in Scheme I. However, by comparing the UV spectra of "magic-acid"-protonated ketones with those of corresponding alkyl cations, Olah et al.[6,7] have concluded that the hydroxy-allyl forms (b and c) are only minor contributors, with a being predominant. Two of the ions in these solution studies were among our photodissociation series, and Table II

$$ \diagdown\!\!\diagup\!\!\diagdown\!\!\diagup^{OH^+} \longleftrightarrow \diagdown\!\!\diagup\!\!\diagdown\!\!\diagup^{OH} \longleftrightarrow \diagdown\!\!\diagup\!\!\diagdown\!\!\diagup^{OH} $$

$$ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\oplus\qquad\qquad\qquad\qquad\oplus $$

$$ \underline{a} \qquad\qquad\qquad\qquad \underline{b} \qquad\qquad\qquad\qquad \underline{c} $$
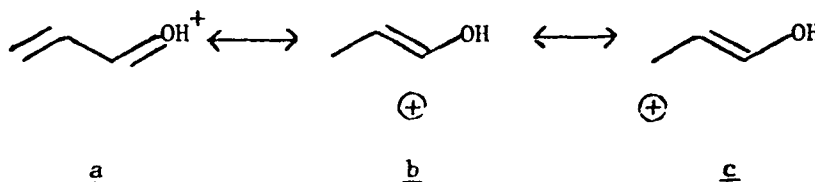
Scheme I

compares gas phase and solution results. Considering the substantial solvent shifts seen in the neutrals, it is surprising that no significant shift in the ion peaks is seen on going from the gas phase to a strong-acid medium. As the table shows, there is a decrease in ΔPA on going from gas phase to solution. Taking the point of view that the higher proton affinity of the excited state arises from higher coulomb attraction from the localized negative charge density on the oxygen, it is understandable that, in solution, these coulomb forces would be attenuated by the higher dielectric constant, leading to a leveling of ground and excited state proton affinities.

TABLE II

	$\lambda_{max}(g)$	$\lambda_{max}(soln)$	ϵ (soln)	ϵ (gas)	ΔPA_{gas}	ΔPA_{soln}[a]
	280	284			1.17	.80
	340	340 270	21×10^3 6×10^3	13×10^3	1.34	1.03

[a] These values are based on methanol spectra as neutral spectra in magic acid are not known. A further red-shift is expected on going from methanol to magic acid and therefore the ΔPA solution values are upper limits.

As shown in Table II, the gas-phase photodissociation cross sections are smaller than the solution absorption cross sections: this might indicate a quantum yield for photodissociation less than unity; but in view of the large uncertainties in all the measured numbers, this should not be considered conclusive. For the second compound in Table II the 270 nm peak observed in solution was not seen in the gas phase, suggesting either a low gas phase intensity, or an impurity problem in the solution spectrum.

Theoretical Considerations

Although proton affinities of ground state molecules can now be calculated with useful precision,[8] analogous calculations on excited-state molecules present major difficulties. The $\pi \to \pi^*$ excited state of acrolein derivatives, in particular, gives problems due to the multiple open shell configurations of the same symmetry. However, useful insights can follow from the expected correlation between ground-and excited-state PA's and calculated oxygen charge densities and dipole moments for these states.

The simplest qualitative picture is the "molecule within a molecule" approach, which considers the $\pi \rightarrow \pi^*$ transition as essentially an intramolecular electron transfer from the ethylene to the carbonyl molecular orbitals. This picture suggests an increase in electron density at oxygen in the $\pi \rightarrow \pi^*$ state relative to the ground state, corresponding to an increase in PA which is in accord with our experimental results.

Several extensive calculations have been reported which can give more substance to this primitive argument. Zimmerman et al.[9] report electron densities as in Fig. 8 obtained from configuration interaction calculations on ground and excited states of enone and dienone systems. The expected increase in oxygen charge upon excitation to the $\pi \rightarrow \pi^*$ state is evident. In addition, the calculated prediction that the dienone should show a significantly greater increase in basicity than the enone is supported by our results of greater ΔPA for 4 and 5 than for the enones investigated. Iwata and Morokuma[10] used ab initio methods with several basis sets to obtain ground- and excited-state electron distributions, finding in all cases increases in oxygen charge density upon excitation. On the other hand, Dykstra[11] in his extensive SCF calculations on acrolein obtained a decrease in electron density at oxygen, and a corresponding decrease in dipole moment, for the $\pi \rightarrow \pi^*$ excitation. This latter calculation of the excited state has been criticized on the basis of its substantial non-orthogonality to the ground state,[12] and the fact that its conclusions differ from the other calculations and our results do not seem very disturbing. Thus, the preponderance of theoretical evidence is in accord with the simple picture of intramolecular charge transfer in the $\pi \rightarrow \pi^*$ transition with increased oxygen charge, increased dipole moment and resulting increase in proton affinity. The very large ΔPA from the present experiments lends support to this picture.

Recent calculations[13] and experiments[14] on the neutral acrolein chromo-
phore predict two closely-spaced optical $\pi \to \pi^*$ transitions. The asymmetry
seen in many of the bands for both neutrals and ions may reflect this
possibility, and the suggestion of structured spectra for ions 2, 3, 6 and
7 might be the result of resolving these two transitions. Calculations[13]
predict that the two transitions are affected differently by substituents,
and they may very well react differently to protonation.

It is possible to rationalize the experimental results using perturba-
tion arguments. Protonation stabilizes the $\pi \to \pi^*$ excited state more than
the ground state because it allows a delocalization of negative charge
accumulation at the oxygen, which is greater in the excited state. Methyl
groups and extended conjugation perform a similar function by stabilizing
the increased positive charge experienced by the carbon atoms. Both of
these effects cause red-shifts, but since they act on different regions of
the molecule, one might, in a first order approximation, expect them to be
additive, that is, independent of each other. To the extent that this is
true, we expect the ΔPA values to be the same for the whole series. The
moderate variations observed in ΔPA's reflect a breakdown in this approxi-
mation, and therefore this cross interaction of the two red-shifting per-
turbations should be considered as a second order effect. Substitution
and extended conjugation can change the oxygen charge density and thereby
affect the ability of the proton to stabilize the molecule, with a resulting
variation in ΔPA values.

Conclusion

This work has consisted of examining the photodissociation spectra of protonated ions and comparing them to absorption spectra of the corresponding neutrals and available solution spectra of ions. The photodissociation results are an effective route to obtaining reliable gas phase absorption information without the hindrance of solvent effects. Interpretations were made concerning the varying effects of different substituents on the excited state of the much studied acrolein chromophore. These substituents are also responsible for the lack of a solid correlation between ion and neutral from a ΔPA standpoint.

The results are very encouraging in terms of carrying over the regularities of the "Woodward rule" point of view from the neutral to the corresponding ions. If substituent effects were identical in neutrals and ions, the ΔPA values in Table I would all be the same, and, for a given type of substituent, this has been seen to be the case. The modest changes in ΔPA values between the three classes of compounds studied indicate that somewhat different values of the Woodward-rule parameters will be appropriate for ions.

From an analytical point of view, photodissociation spectroscopy of the protonated molecules offers the very useful possibility of optical analysis of samples on the mass-spectrometric sensitivity scale (potentially 10^{-12} g), with the photodissociation spectrum providing the usual spectroscopic structure clues.
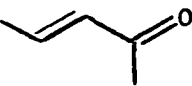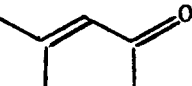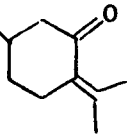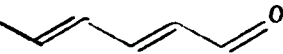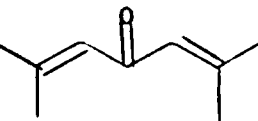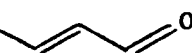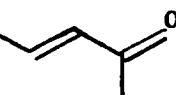
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TABLE I

		λ_{max}		
		Ion	Neutral	ΔPA[b] (eV)
1.		262 nm (2.4)	210 nm	1.17
2.		280 nm	224 nm	1.11
3.		308 nm	237 nm	1.20
4.		340 nm (4.6)[a]	246 nm	1.39
5.		339 nm (5.0)[a]	248 nm	1.34
6.		378 nm / 410 nm	262 nm	1.45 / 1.68
7.		392 nm / 410 nm	265 nm	1.52 / 1.66

---

[a] λ_{max} Photodissociation cross sections(σ) in units of $10^{-17} cm^2$

[b] Uncertainty $\pm$ .03 eV

Figure Captions

Fig. 1 -- 3-pentene-2-one: photodissociation spectrum of protonated
ion (-●-) compared to the neutral absorption spectrum
(—).

Fig. 2 -- Mesityl Oxide (as in Figure 1).

Fig. 3 -- Pulegone (as in Figure 1).

Fig. 4 -- 3,5-hexadienal (as in Figure 1).

Fig. 5 -- Phorone (as in Figure 1).

Fig. 6 -- Cinnamaldehyde (as in Figure 1).

Fig. 7 - 4-phenyl-3-butane-2-one (as in Figure 1).

Fig. 8 -- Calculated π electron densities of enone and dienone
systems as taken from Ref. 9.

Figure 1
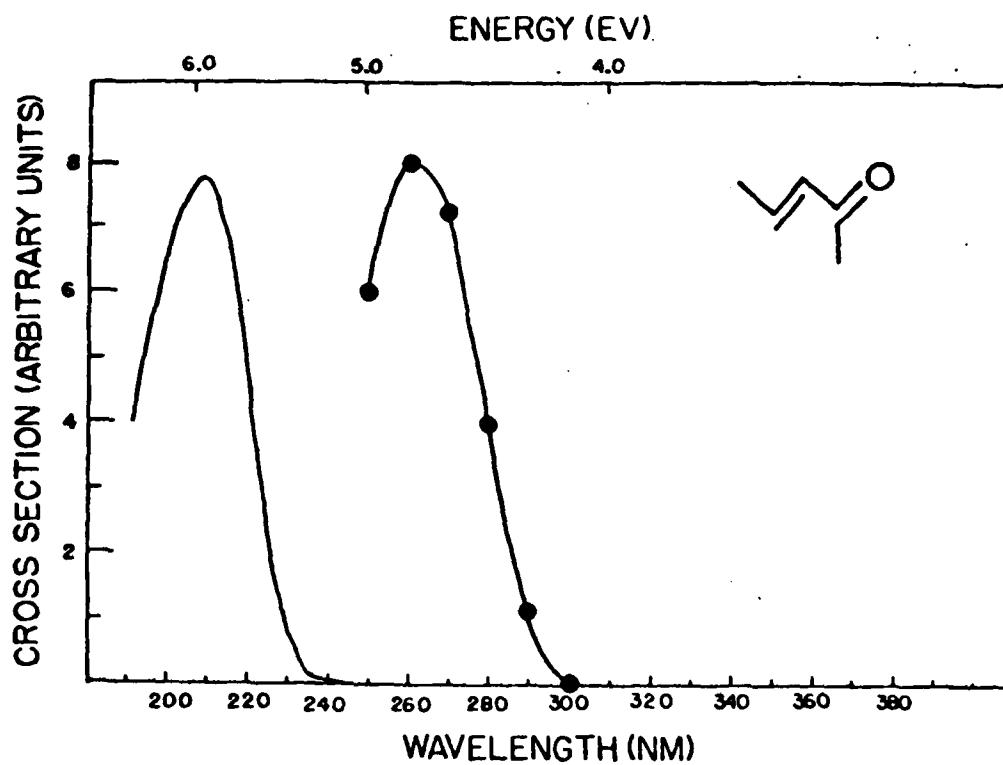
Figure 2
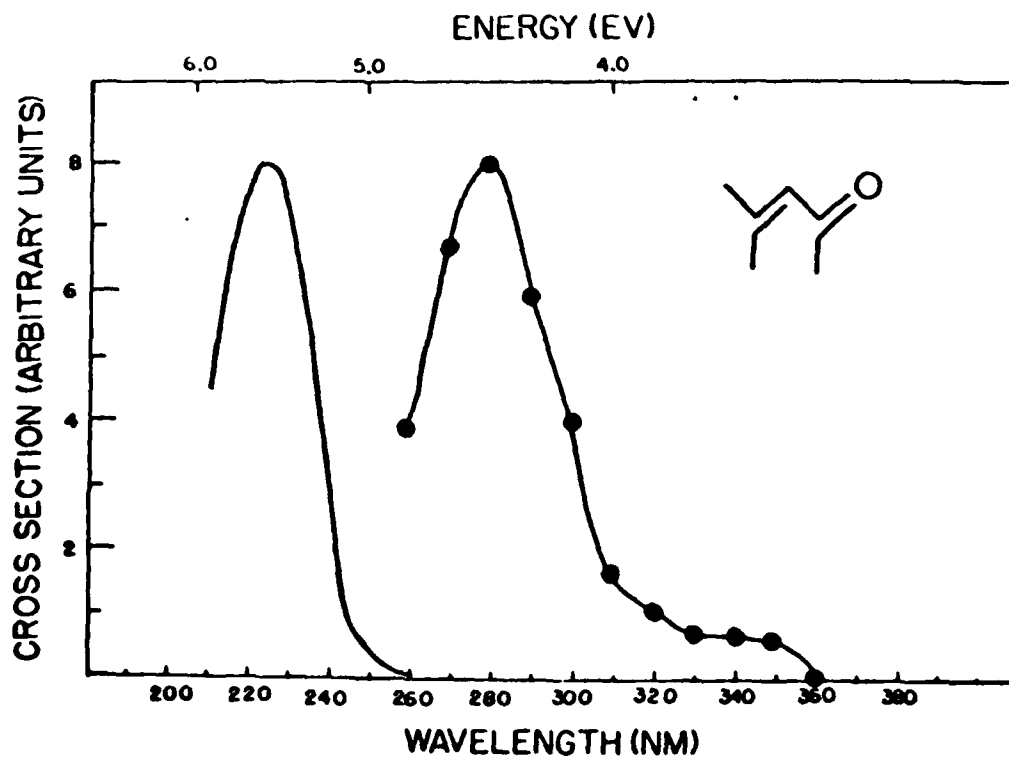
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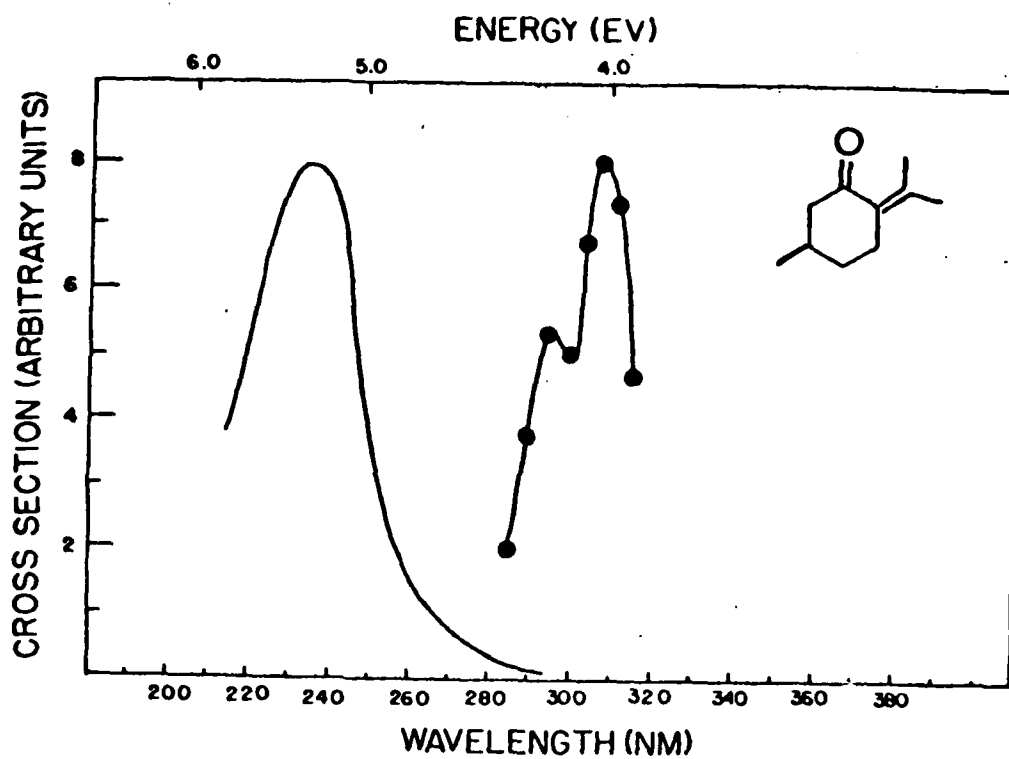
Figure 4

Figure 5

Figure 6

-49-
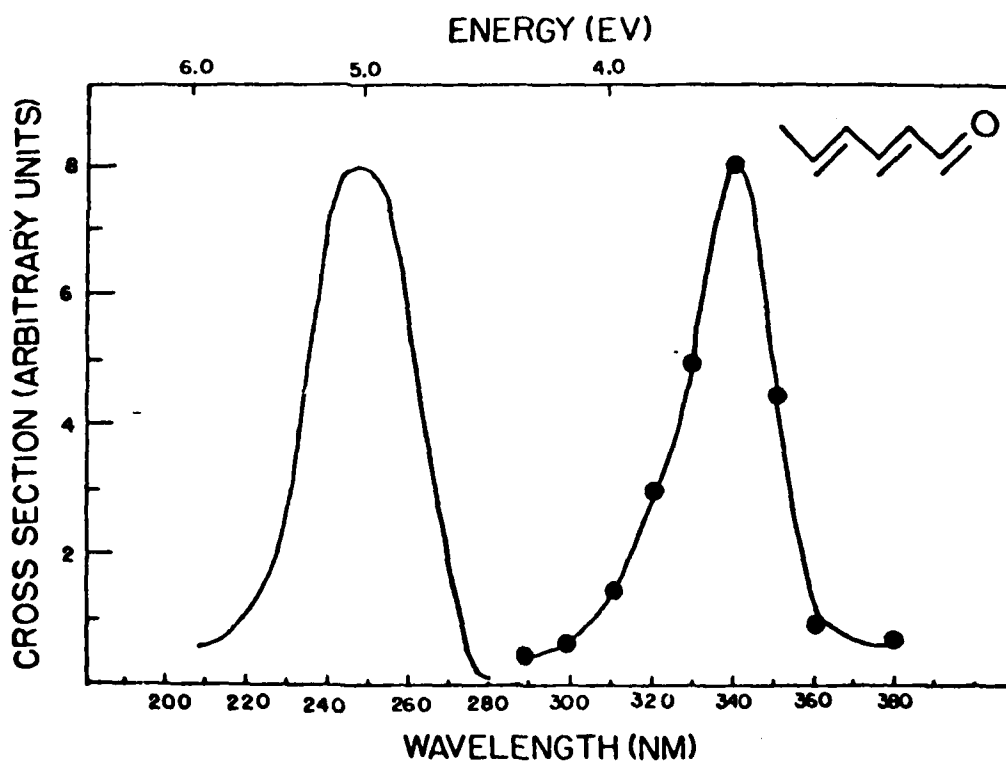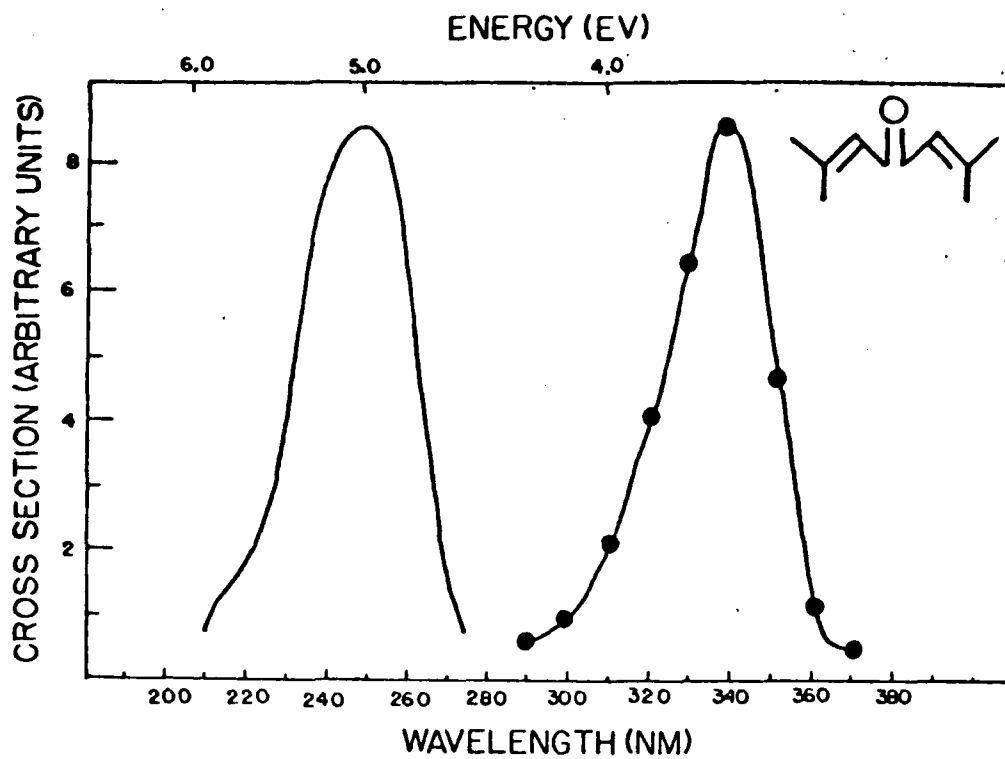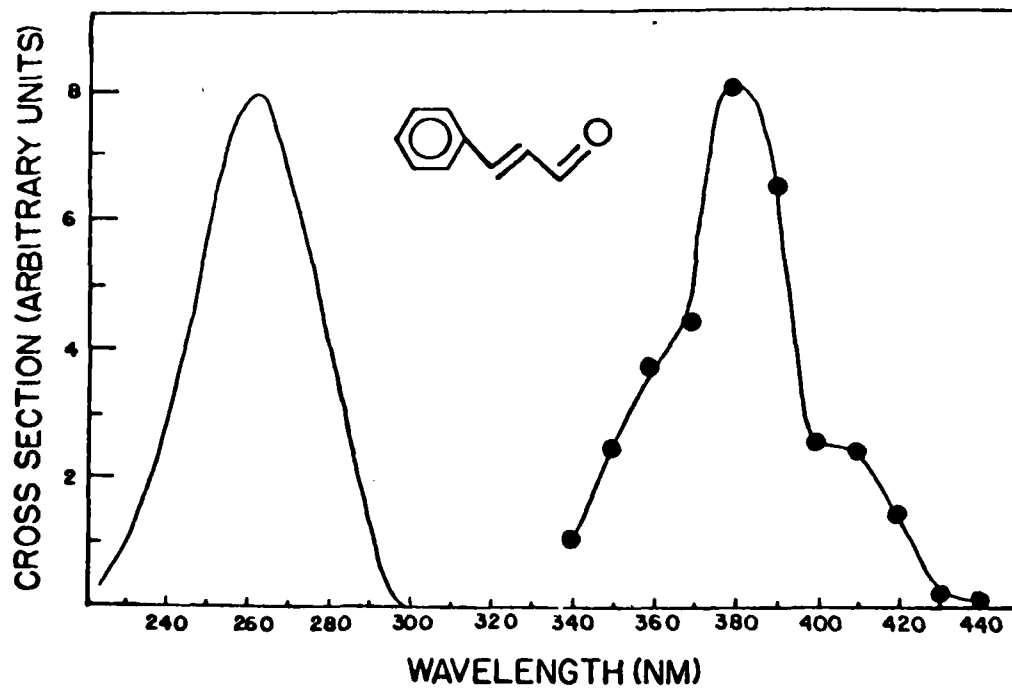
Figure 7
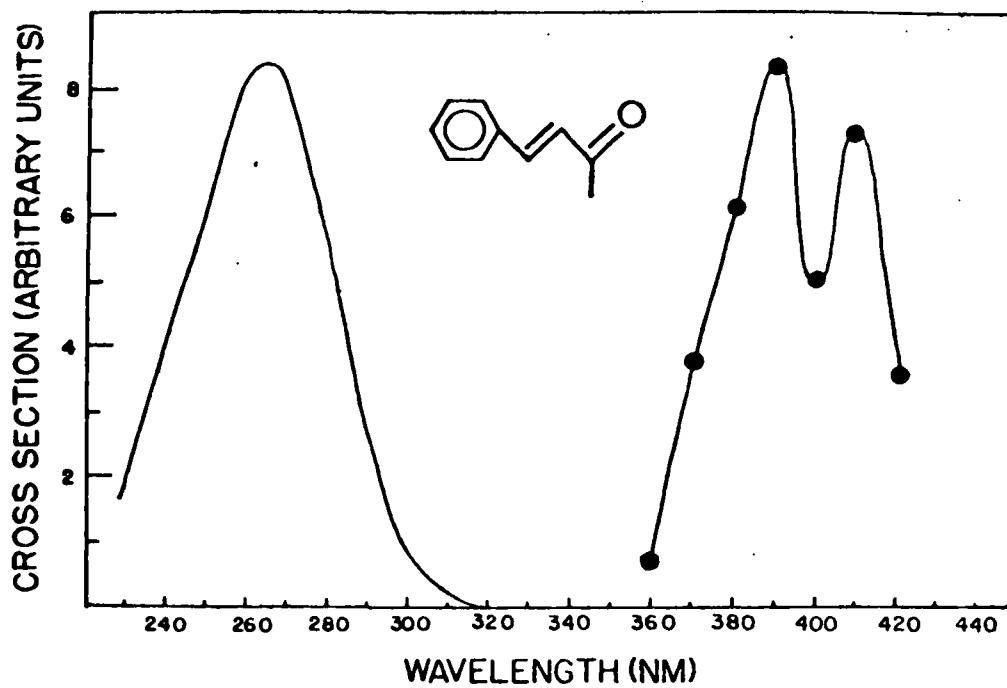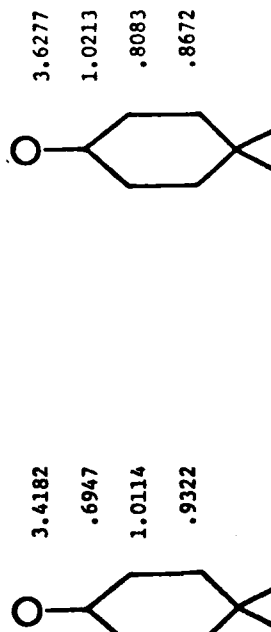

Figure 8

CALCULATED π ELECTRON DENSITIES

GROUND STATE

π* EXCITED STATE

APPENDIX B

Photodissociation Spectroscopy of Hexadiene Radical Ions:

Structural Rearrangements in the Gas-Phase Ions

by

Robert C. Benz, Robert C. Dunbar and

Paul C. Claspy

Abstract

Photodissociation spectroscopy was applied to determining the structure of ions formed by electron impact ionization of hexadienes. 1,3-hexadiene and 2,4-hexadiene gave distinguishable spectra typical of conjugated diene radical cations. 1,4-hexadiene gave a spectrum identical with 2,4-hexadiene ions, indicating complete rearrangement of the double bond into conjugation. However, 1,5-hexadiene gave an entirely distinct spectrum characteristic of unconjugated olefin cations. The laser photodissociation spectra of the three cis-trans isomers of 2,4-hexadiene ions were readily distinguishable, indicating that rotation around the double bond in the radical cation is not facile. The rearrangement of 1,4-hexadiene ions appeared to yield a mixture of cis-cis, cis-trans, and trans-trans structures. MINDO/3 calculations support the observed shift in peak positions among the three cis/trans isomers of 2,4-hexadiene ion. The spectrum of 1,3-hexadiene suggested the retention of cis/trans isomerism.
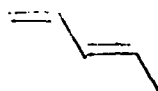
Photodissociation Spectroscopy of Hexadiene Radical Ions:

Structural Rearrangements in the Gas-Phase Ions

INTRODUCTION

Ionization of an unsaturated hydrocarbon will normally involve removal
of a pi electron, and the resulting weakening of the pi bonding system can
be expected to increase the lability of the molecule to various rearrange-
ment processes. One such rearrangement which has been of interest is the
migration of double bonds into conjugation, and some recent results using
photodissociation spectroscopy to characterize the structures of the radi-
cal cations have suggested that migration of a double bond by one position
is easy, while migration across two or more positions can involve substan-
tial energy barriers.[1] Another rearrangement, cis-trans isomerization
around a double bond, is no less interesting, but has been harder to study
because of the usually small spectroscopic changes accompanying cis-trans
isomerization. The hexadienes have proven to be exceptionally tractable
compounds for investigation of both of these questions by photodissociation
spectroscopy,[2] and we describe here the picture which has been obtained of
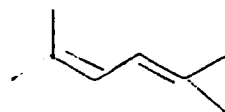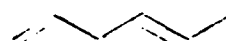these rearrangement processes involving the hexadiene isomers 1, 4, 5
and 6.

1a

1b

1c

2

3

4

5

6

EXPERIMENTAL

Photodissociation spectra[2] were obtained in the UV and visible

region of the spectrum for each of the 2,4-hexadiene isomers, and for

mixed-isomer samples of the 1,3 and 1,4 isomers and 1,5-hexadiene. The

UV region was studied using light from a 2.5 KW Hg-Xe arc lamp with the

wavelengths selected by a Schoeffel grating monochromator with two 2 mm

slits (nominal band-pass (FWHM) of 6.6 nm). The monochromator was also

used without slits with a bandwidth (FWHM) estimated to be $\sim$ 40 nm for

the study of 1,5-hexadiene cations. This was necessitated by the lower

absolute cross section of the UV peak. The visible region was first

analyzed with interference filters to locate the position of the photo-

dissociation peak, then the region containing the peak was studied using

a Chromatix CMX-4 pulsed dye laser. All of the visible peaks fell within

the range of coumarin 480 (coumarin 102) dye 4840 Å – 5140 Å, so all the

isomers could be compared directly with each other. The absolute cross

sections were estimated for all isomers by measuring the photodissociation

rate at 360 nm immediately after measuring the photon flux at that wave-

length. The photon flux was determined by observing the photodissociation

rate of 2,5-dimethyl 2,4-hexadiene (3), which has a known absolute cross sec-

tion at 360 nm of 5×10^{-17} cm^2. This technique of determining absolute

cross sections has been used extensively and is considered to give abso-

lute cross sections within a factor of two.

All of the conjugated cations examined here have absolute cross

sections of 5×10^{-17} cm^2 for the UV peak, and the 1,5-hexadiene cation

peak was estimated to be 5×10^{-18} cm^2. The percent error associated

with the relative cross section values is $\pm 20\%$. The absolute cross sec-

tions of the visible peaks were determined by comparing the photodissoci-

ation rate at several wavelengths selected by the monochromator in both the UV and visible regions. The relative flux of the arc lamp monochromator source at these wavelengths has been determined by Eppley thermopile measurements. The value of the visible peak absolute cross section is 1×10^{-17} cm^2 for all of the conjugated ions. The visible region of 1,5-hexadiene cation was examined extensively with both the filters and the laser in the region of the conjugated diene peak and no photodissociation ($<10^{-19}$ cm^2) was observed.

The sample of 1,3-hexadiene used was a mixture of 3-cis and 3-trans isomers obtained from Chem. Samples Co. as were all of the hexadiene samples. Therefore, the spectrum in Fig. 3 is actually a composite spectrum of the two isomers. The sample of 1,4-hexadiene was also a mixture of 4-cis and 4-trans isomers so the spectrum in Fig. 4 is also a composite. The three isomers of 2,4-hexadiene were studied separately and their spectra are shown in Fig. 2.

RESULTS AND DISCUSSION

Spectra of the Conjugated Diene Ions

The ground state conjugated diene radical cations have a vacancy in the highest occupied π molecule orbital (HOMO). As illustrated in Fig. 1, the ion photodissociation spectrum typically has two peaks in the visible-UV region: the higher energy peak has usually been considered to reflect excitation of the single electron from the HOMO into the lowest unoccupied π* orbital (LUMO), in a transition denoted as type A.[3,4] The lower energy peak is usually considered to be a hole-excitation transition, denoted type I, involving excitation for an inner electron into the vacancy in the half-filled HOMO. This is the assignment of the two photodissociation peaks of conjugated diene radical cations which was first proposed for butadiene[5] and later for various other dienes,[2c] and it has received support from several theoretical studies.[3,4,6]

Substitution of methyl groups on the butadiene skeleton gives a regular pattern of spectral shifts. The low-resolution photodissociation spectrum of butadiene cation (2)[5] gives peaks at $(2.32 \pm .04)$ eV and (4.0 ± 0.1) eV. In 2,4-hexadiene (1,4-dimethyl butadiene) (1) these peaks shift to $(2.50 \pm .04)$ eV and (3.7 ± 0.1) eV (mixed-isomer spectrum).[2b] In 2,5-dimethyl-2,4-hexadiene ion (1,1,4,4-tetramethyl butadiene) (3) the peaks shift further to $(2.65 \pm .02)$ eV and (3.4 ± 0.1) eV.[2b] There is thus an apparently regular methyl shift to the blue of ∿.08 eV per methyl group in the I transition, and a shift to the red of 0.15 eV per methyl group in the A transition, upon terminal-methyl substitution of butadiene ion. The visible photodissociation peaks in these three ions are similar in shape, and all have a width (FWHM) of ∿0.4 eV, while the UV peaks, also similar in shape and markedly asymmetrical, have a width of ∿0.6 eV.

The position of the I transition can be usefully compared with the photoelectron spectroscopic assignment of the energies of the ground and first excited states of the ions, as has been discussed in detail.[5] The most defensible comparison is to compare the optical peak position with the difference between the adiabatic first IP and the vertical second IP. (In this case, only for 3 do the adiabatic and vertical IP's differ.) The agreement is satisfactory,[7] within the uncertainty, for ions 1, 2 and 3.

The I transition can also be correlated with molecular orbital calculations of the highest two occupied orbital energies. MINDO/3 calculations[8] (using model geometries and a statistical weighting of 2,4-hexadiene isomers) were made to test the ability of the MINDO parametrization to predict the shift in I peak position between 1 and 2. The calculation yielded a predicted blue shift of 0.16 eV in going from butadiene to 2,4-hexadiene, in excellent agreement with the observed shift of 0.18 eV. This lends some confidence to the more exacting demands made on the MINDO program in the section on cis/trans isomerization. (It may be noted that the SPINDO parameterization of the INDO method[6] predicts a red shift in this case, and it appears that the MINDO program, while not yielding as good absolute orbital energies as SPINDO, may be preferable in assessing the perturbing effects of substituents on the high-lying occupied orbitals.)

Bond Migrations

The photodissociation spectra of the hexadienes shown in Figures 2-5, give clear evidence on the possibilities of bond shifts following electron-impact ionization of the neutrals.

It is clear from Fig. 5 that 1,5-hexadiene (6) does not rearrange appreciably to any conjugated structure, its spectrum being entirely characteristic of unconjugated olefin radical ions, but wholly unlike conjugated diene spectra.[2b] The lack of photodissociation around 500 nm sets a limit

on the possible extent of rearrangement of less than 1%. The spectrum is also unlike that of cyclohexene ion.

Comparison of Fig. 3 with Fig. 2, particularly the UV peaks, suggests that the 1,3 (4) and 2-4 (1) isomers retain distinct structures. While the differences in the spectra are modest, and a partial rearrangement of the order of 25% cannot be ruled out, it is quite clear that complete rearrangement does not take place. Since the 4 → 1 rearrangement seems an unlikely process in any event, it appears reasonable to conclude that no interconversion of these isomers occurs.

On the other hand, the 1,4 isomer (5) evidently rearranges into conjugation, as indicated by the close similarity of Fig. 4 to Fig. 2. The UV peaks are identical in shape and cross section, and the visible peaks are very similar. Judging from the PES spectra of 1,4 dienes,[9] the I transition in unrearranged 5 would lie far to the red, near 2500 nm, and its spectrum would be entirely unlike that of 1 or 4, so that the appearance of Fig. 4 is conclusive evidence that 5 rearranges into conjugation. The UV peak of 5 is much more similar to that of 1 than 4, so that the more stable 2,4 isomer 1 is evidently the preponderant rearrangement product. It is tempting to match the maxima in the visible spectrum of Fig. 4 to the three cis-trans isomers of 1, and say that the rearrangement yields 1a, 1b and 1c in the approximate ratio 3:2:1. As is seen below, the position and spacing of the three visible-region maxima in Fig. 4 are consistent with this suggestion. Judging both from the absence of photodissociation at wavelengths below 280 nm, (where strong photodissociation is expected for simple olefins and unconjugated dienes), and from the identity of the cross section in Figures 4 and 2, the rearrangement 5 → 1 is complete upon ionization. The spectrum obtained for 5 remains the same over a wide range of pressures, trapping times and ionizing voltages, and even under conditions

allowing a number of ion-molecule collisions there is no evidence of any
ions retaining the unconjugated structure.

Cis-Trans Isomerization

As is clear in Fig. 2, the visible peaks in the spectra obtained for
the ions of the three cis-trans isomers of 2,4-hexadiene are definitely
distinct. Before concluding that rotation about the double bonds does
not occur, however, the possibility must be excluded that the differences
arise not from structural differences in the ions, but from differing internal
energies, with the hot bands associated with larger internal energies shifting
the absorption to longer wavelength. There are several lines of argument
against the latter possibility: First, it could be argued that more internal
energy would be deposited in the isomer with lower ionization potential; based
on the IP's from PES spectra[9] this would suggest a wavelength order 1c > 1a
> 1b, instead of the observed order 1c > 1b > 1a. Second, if the shift to
long wavelength for 1c is due to larger internal energy, it should be pos-
sible to shift the peak by collisional relaxation of the ion. However,
there was no change in the spectrum of 1c when the conditions were varied
from 1×10^{-8} torr, 1 second trapping to 1×10^{-7} torr, 10 second trapping,
which corresponds to a calculated number of ion-neutral collisions during
the trapping period increasing from about 1 to 100. Figure 6 shows one
such comparative pair of spectra which clearly show no tendency for the
long-wavelength absorption to diminish with increasing numbers of collisions.
Under these high-pressure, long trapping conditions, charge-transfer relaxa-
tion, non-reactive collisional relaxation and IR radiative relaxation
would be expected to be effective in reducing any substantial amount of
internal energy of the ion.

Further evidence that the photodissociation results in fact reflect
structure retention comes from molecular orbital calculations of the π-

orbital separation. While, as indicated above, these MINDO/3 calculations should not be asked to give highly precise orbital spacings, it is reasonable to expect a good reflection of the small orbital perturbations corresponding to the different cis/trans configurations. The MINDO/3 result is an ordering of the π-π orbital separation for the three isomers of 1c < 1b < 1a, with an interval of .03 eV between each neighboring pair. In Table I the three peak positions for the high-resolution laser spectra are given, along with the intervals from the molecular orbital calculations; both the experimental and theoretical results suggest that the π-π orbital separation increases by about .03 eV for each cis double bond in the molecule.

We conclude that the observed spectral differences between the three isomers of 1 do actually reflect distinct structures, and that cis-trans interconversion is not complete on a time scale of seconds in this series of isomers. This can be compared with what has been found for other cis-trans isomerizations in unsaturated radical ions: the cis and trans isomers of 1-chloropropene ion were clearly shown from their vibrationally resolved photodissociation spectra to retain distinct structures.[10] The cis and trans isomers of 1,3,5-hexatriene ion give distinct fluorescence emissions,[11] indicating little interconversion on the fluorescence time scale (10^{-8} sec), but on the ICR time scale of seconds, only the photodissociation spectrum of the cis isomer is observed,[12] possibly indicating rearrangement of this time scale.

The spectrum of 1,3-hexadiene ion (4) in Fig. 3 not only shows clearly that rearrangement to the more stable 1 does not occur, but also suggests retention of the two cis/trans isomer structures. Only a mixed-isomer spectrum of 4 was obtained, but the visible spectrum in Fig. 3 suggests two

separate peaks. The separation of about .04 eV (8 nm) between these maxima

is in accord with the shifts found for the 2,4 isomers, and it seems reason-

able to take this spectrum as showing the presence of both cis/trans isomers.

CONCLUSIONS

The experimental results indicate that there is no rotation around the double bonds in the ionization of 2,4-hexadiene isomers. Each ion structure has a unique photodissociation spectrum, and spectral differences are in accord with the molecular orbital calculations. The spectral differences of the 2,4 isomers are greater in the visible region than those seen for the 1-chloropropene isomers,[10] and there are also differences though smaller, in the UV region. It would be of interest to reexamine the two isomers of 2-butene[13] at a higher spectral resolution to see if the two spectra are really identical or if there is a shift too small to be seen at low resolution.

Where rearrangement occurred, in the case of 1,4-hexadiene, the 2,4-hexadiene structure was apparently formed. The double bond shift from 1,4 to 2,4 is similar to that seen in the rearrangement of allylbenzene to 1-phenylpropene[14] and most likely the mechanism of rearrangement involves a 1,3-hydrogen shift.[15]

There is no evidence of any conjugated ions formed from 1,5-hexadiene, which is consistent with results for the unconjugated phenylalkenes.[14] A double bond shift of two positions has not been observed in any spectra except for 1,5-octadiene.[16] In that case the amount of rearrangement has been estimated to be 30% and must occur as a result of the cyclic nature of the chain.

References

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(2) For description of these techniques, see for instance: (a) Dymerski, P. P.; Fu, E.; Dunbar, R. C. J. Am. Chem. Soc. 1974, 96, 4109; (b) Dunbar, R. C. Anal. Chem. 1976A, 48, 723; (c) Benz, R. C.; Dunbar, R. C. J. Am. Chem. Soc. 1979, 101, 6363.

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(14) Fu, E. W.; Dunbar, R. C. J. Am. Chem. Soc. 1978, 100, 2283.

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Figure Captions

1. Photodissociation spectrum of 2,4-hexadiene ion (1) at ∿10 nm resolution.

2. Laser photodissociation spectrum in the visible, and monochomrator spectrum at 6.6 nm resolution in the UV, of the three isomers of 2,4-hexadiene ion (1a, b, c).

3. Laser spectrum in the visible and monochromator spectrum in the UV of 1,3-hexadiene ion (4).

4. Laser spectrum in the visible and monochromator spectrum in the UV of ions obtained from ionization of 1,4-hexadiene (5).

5. Monochromator spectrum at ∿40 nm resolution for 1,5-hexadiene ion (6).

6. Interference-filter spectra of ion 1c. (•) shows the spectrum at 4 seconds *trapping time* and $3x10^{-8}$ torr. (▲) shows the spectrum at 10 seconds trapping time and $1x10^{-7}$ torr.

ORBITAL SPACING FOR 2,4 HEXADIENE ISOMERS

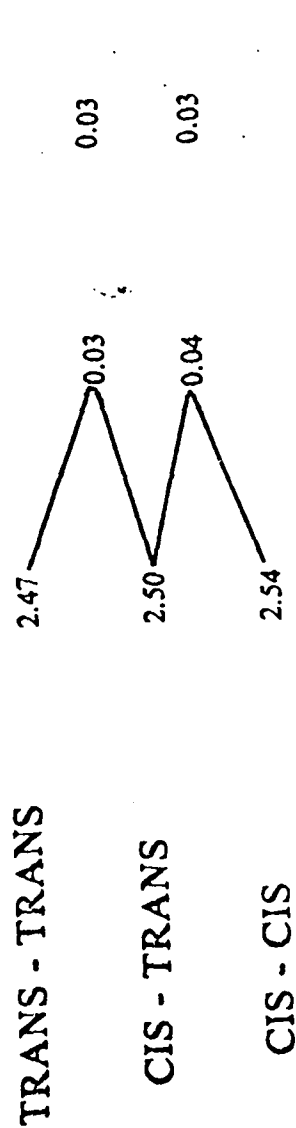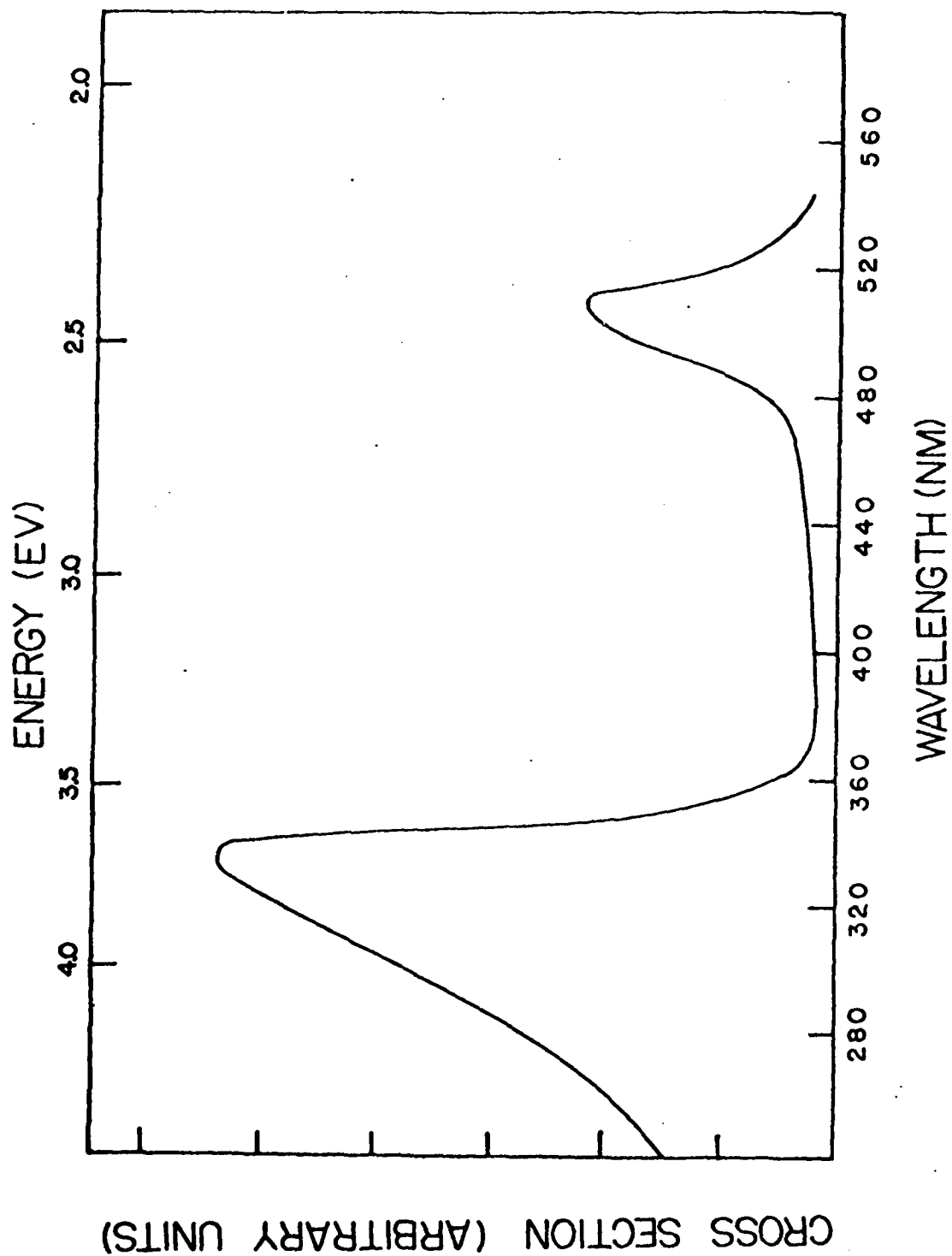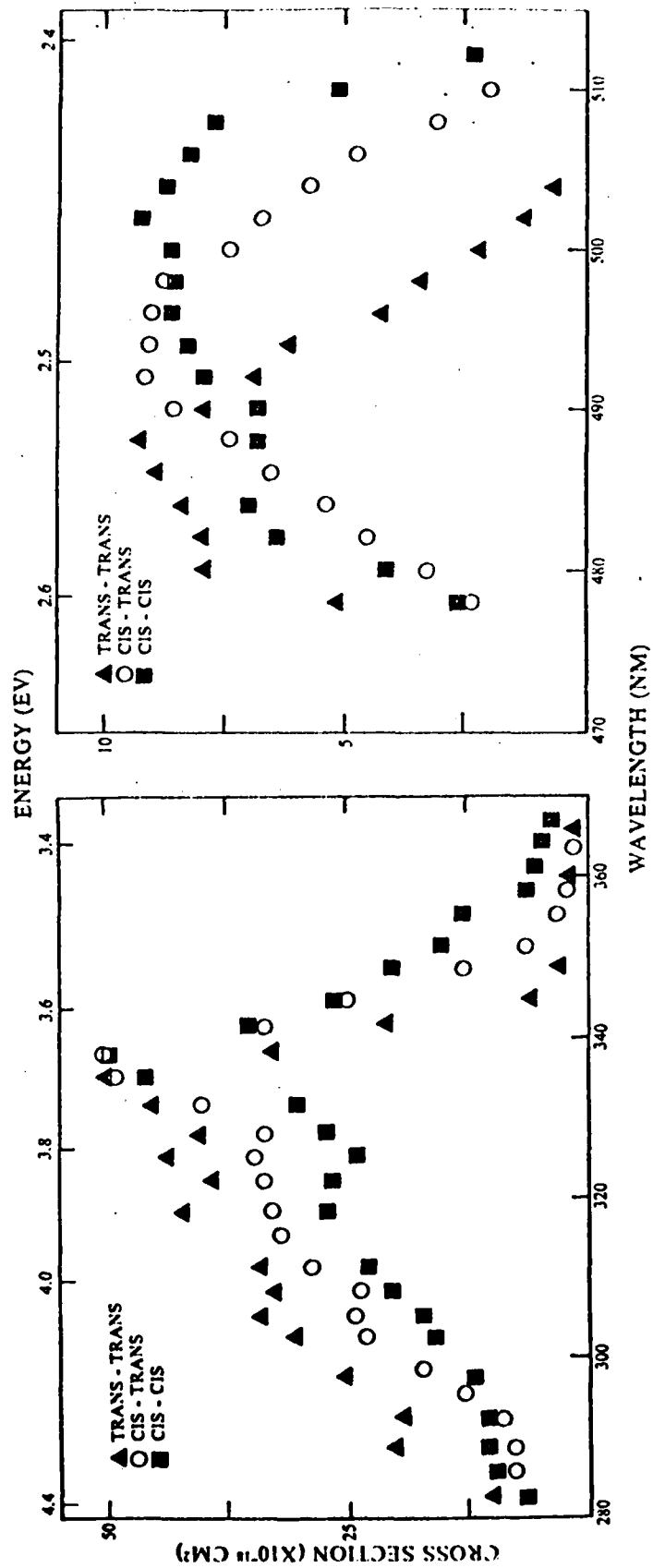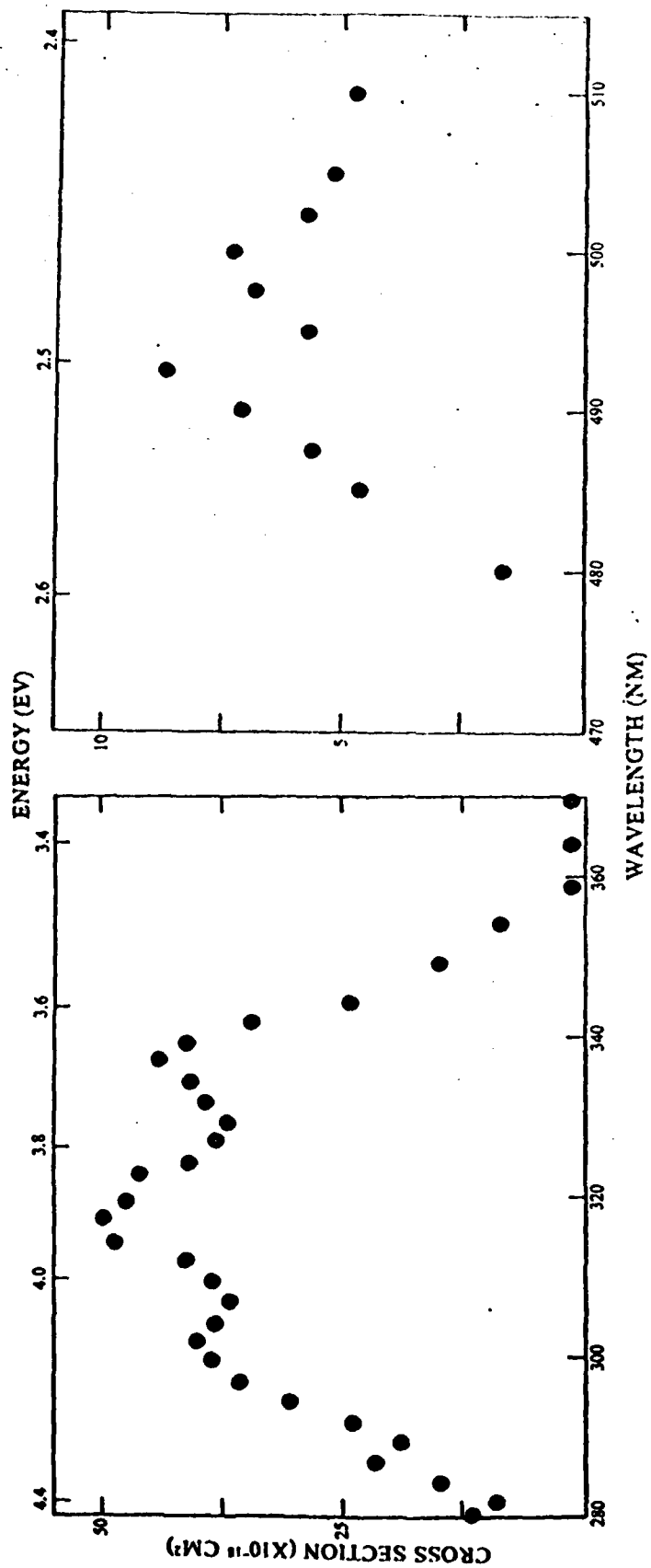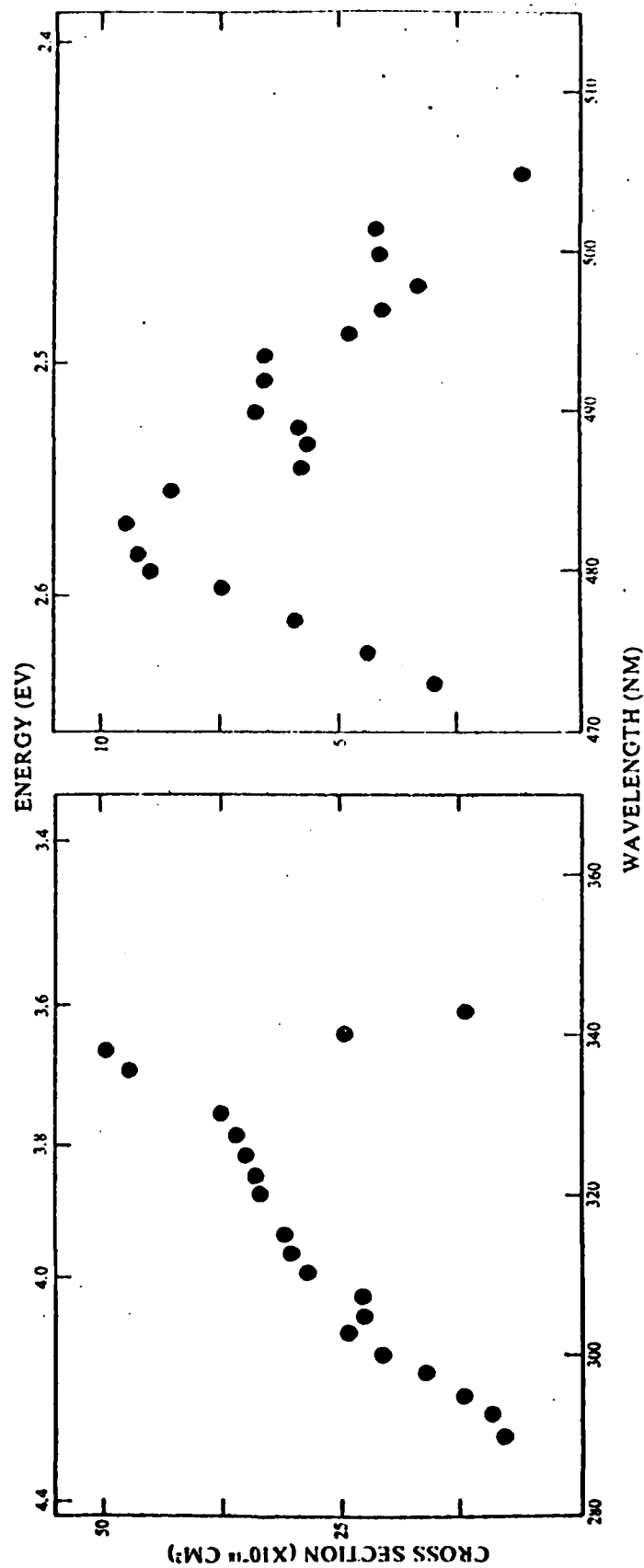|	SPECTRAL PEAK POSITION (EV)	DIFFERENCE (EV)	THEORETICAL (EV)
TRANS - TRANS	2.47	0.03	0.03
CIS - TRANS	2.50	0.04	0.03
CIS - CIS	2.54		

Diagram 1

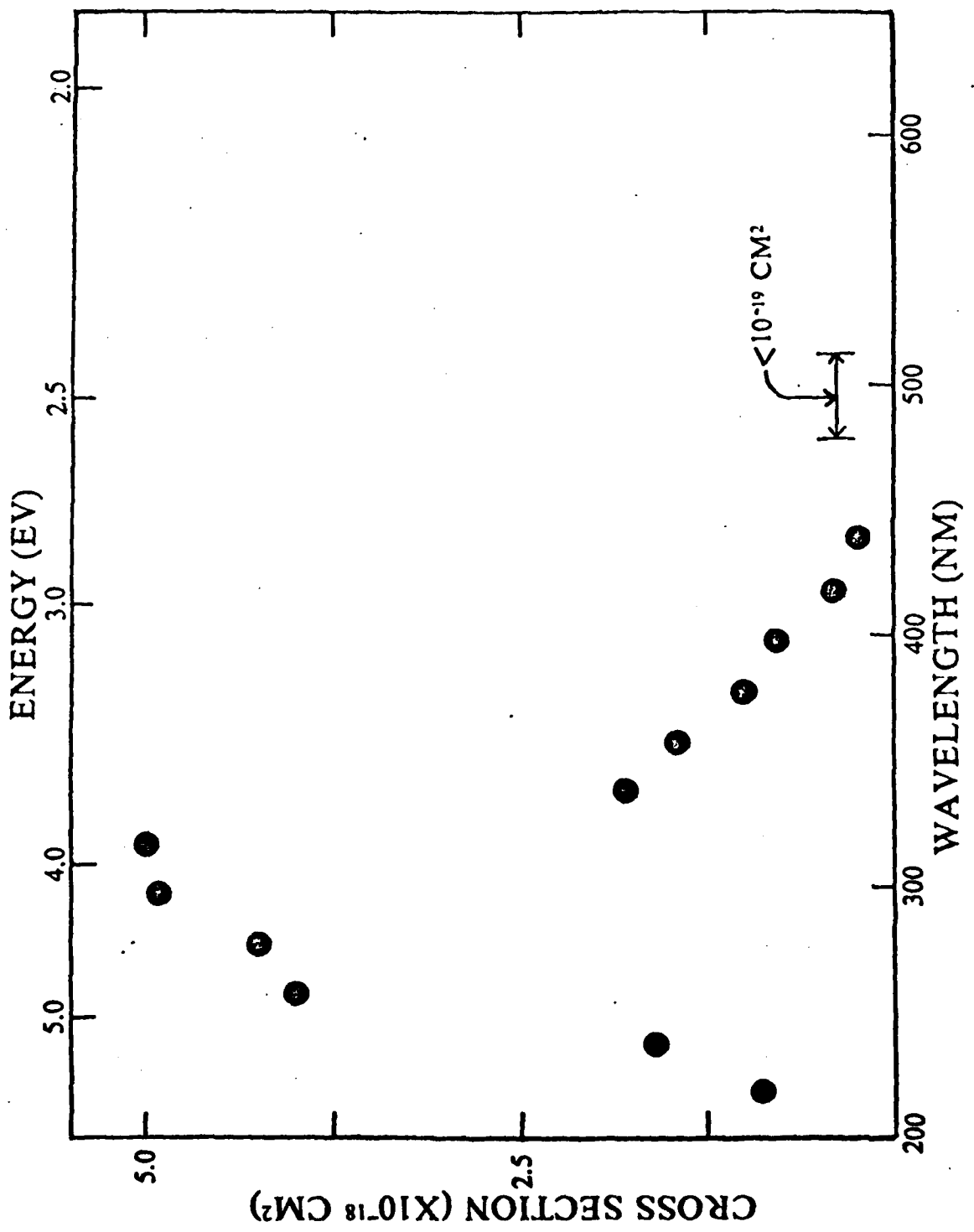PHOTODISSOCIATION SPECTRUM OF 2,4 HEXADIENE

2,4 HEXADIENE ISOMERS

1,3 HEXADIENE MIXED ISOMERS

1,4 HEXADIENE MIXED ISOMERS

1,5 HEXADIENE PHOTODISSOCIATION SPECTRUM

CIS-2, CIS-4 HEXADIENE TIME DELAYED SPECTRUM